PB90-235789

Development of a Sampling Procedure for Large Nitrogen and Sulfur-Bearing Aerosols

Kansas Univ., Lawrence

Prepared for:

Environmental Monitoring Systems Lab., Research Triangle Park, NC

Jun 90

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/3-90/048

2.

3. RECIPIENT'S ACCESSION NO.
PB90 235789/AS

4. TITLE AND SUBTITLE
DEVELOPMENT OF A SAMPLING PROCEDURE FOR LARGE NITROGEN- AND SULFUR-BEARING AEROSOLS

5. REPORT DATE
June 1990

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Civil Engineering Department
University of Kansas
Lawrence, KS 66045

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
CR-814613-01-0

12. SPONSORING AGENCY NAME AND ADDRESS
Atmospheric Research and Exposure Assessment Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Project Report

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A single-stage impactor was modified to utilize a removable TFE impaction surface mounted on the end of an annular denuder. When used with a polycarbonate filter coated with silicone oil, its cut point was 2.5 µm and bounce was <1% for 8-µm particles. Significant bounce occurred with uncoated or grease-coated surfaces. Bounce was about 2% using oil-saturated porous glass disks, but particle extraction was difficult. The best performance was achieved using a vertically mounted impactor with a bent-tube inlet to sample isoaxially. For 2.0-2.8 µm particles, 4-8% of the mass sampled was found in the denuder and 10-17% on the spacer between the impactor and the denuder; internal losses for larger and smaller particles were negligible. Several oils and greases were compatible with ion chromatography. Polycarbonate filters, silicone oil, and Vaseline were free of anionic impurites and adsorbed little, if any, nitrate or sulfate when exposed to high concentrations of HNO_3 and SO_2. NH_4Cl and NH_4NO_3 particles impacted on an uncoated filter did not volatilize. Impacted particles of varying composition were generally unreactive toward high concentrations of HNO_3 or SO_2. Acidic $NaHSO_4$ particles impacted on a greased surface reacted to a limited extent (1.7-3.5%) with NH_3. In a 24-hour field test employing four collocated sampling systems, the precision of the method for coarse-particle nitrate and sulfate was ± 3.4% and ± 3.3%, respectively.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Aerosols, sampling, samplers chemical analysis	Impactors, denuders, acid aerosols	Atmospheric Sciences

18. DISTRIBUTION STATEMENT
Release unlimited; available through NTIS

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
122

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB90-235789

EPA/600/3-90/048

June 1990

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Cooperative Agreement CR-814613-01-0

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Office of Research and Development
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U.S. DEPARTMENT OF COMMERCE
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ABSTRACT

Accurate measurement of the individual chemical species associated with dry deposition requires a system capable of quantitatively sampling both particles and gases in ambient air. Many attempts to develop such a system have failed to prevent volatilization of the captured particles, reactions between gases and particles, or reactions between gases and various components of the sampling system. One system currently under development and potentially able to circumvent these problems consists of a filter pack preceded by one or more annular denuders and a Teflon-coated glass impactor. The filter pack is designed to capture fine particles and any gases that may volatilize from them, while the denuders capture reactive gases and allow fine particles to pass through unaltered into the filter pack. The impactor is designed to remove large particles (i.e., those having an aerodynamic diameter greater than 2 μm), which might otherwise be trapped in the denuder or which, if they were alkaline, might neutralize acidic aerosols captured by the filter pack.

Unfortunately, questions have remained regarding the sampling and collection efficiency of the glass impactor for large particles, its particle bounce characteristics (when uncoated, oiled, or greased), its mass loading limitations, its ability to prevent chemical reactions between gases and impacted particles, and the extent to which chemical artifacts form on the impaction surface itself. The objective of this research project was to develop a sampling procedure that would permit accurate chemical and gravimetric analysis of large particles, especially those containing nitrogen and sulfur species of interest, without interfering with sampling and analysis of gases and fine particles. Although other sampling devices were initially considered, the experimental work focused exclusively on a single-stage impactor modified to utilize a removable impaction surface mounted on the end of the first annular denuder. This modified design was first developed as part of another project previously funded by the U.S. EPA; and although it had not yet been fully characterized, it was subsequently incorporated into sampling systems used by several other teams of investigators.

The cut point of the modified impactor, when used with a membrane filter coated with 5 μL of silicone oil, was determined to be 2.5 μm. Less than 1% particle bounce occurred when using oiled membrane filters; but significant particle bounce was found to occur when using uncoated or grease-coated impaction surfaces or when using a porous glass impaction surface. Saturating a porous glass impaction disk with oil reduced particle bounce to about 2%, but the impacted particles could not be easily removed from the porous glass impaction surface. Sudden increases in flowrate caused impacted particles to be dislodged from uncoated or greased surfaces and to migrate away from the center of oiled impaction areas.

Non-isoaxial sampling resulted in substantial undersampling of large particles, so isoaxial sampling (perhaps using a vane-mounted system) appears to be a necessity. Isoaxial sampling of ambient air requires either a horizontally mounted sampling system or a vertically mounted system with an inlet bend. The horizontal configurations tested performed poorly because greased and lightly oiled surfaces exhibited a high degree of particle bounce and oil tended to flow sideways off oil-saturated disks. Vertically mounted systems employing a 90° bent-tube inlet performed reasonably well, but inlet losses were quite high for very large particles (e.g., 91 to 96% for 26.5-µm uranine particles) and for blunt-tipped inlets (e.g., 7-14% for 8-µm uranine particles). Inlet losses averaged only 2.7% for 7.9-µm uranine particles sampled using a sharpened bent-tube inlet in an upright position; the pattern of the deposited particles indicated the presence of a double vortexing flow condition, which did not appear to adversely affect impactor performance.

Losses of solid particles within the combined impactor denuder system (excluding the inlet) were greatest for particles about the size of the cut point. For particles having an aerodynamic diameter of 2.0-2.8 µm, losses in the denuder ranged from 4-8% of the mass sampled, while losses on the spacer between the impactor and denuder ranged from 10-17% of the mass sampled. However, losses for particles of other sizes (larger and smaller) were generally negligible (i.e., <1%).

A number of oils and greases were found to be compatible with the analysis of impacted particles using ion chromatography, i.e., they generally did not leach or sorb significant amounts of the anions of interest. Polycarbonate filters were found to be free of nitrate, nitrite, and sulfate. Polycarbonate filters, silicone oil, and Vaseline exposed to high concentrations of HNO_3 and SO_2 were found to adsorb little, if any, nitrate or sulfate. TFE impaction disks may adsorb HNO_3, but it is not necessary to include them in the analysis if they are overlain by a polycarbonate filter.

Impacted particles of varying composition were exposed to high concentrations of potentially reactive gases (HNO_3, SO_2, or NH_3) at room temperature (69-80°) and low relative humidity (19-48%) for four hours at a nominal flowrate of 16.7 Lpm. Ammonium-chloride and ammonium-nitrate particles impacted on an uncoated polycarbonate filter did not volatilize when exposed to purified air. Ammonium-chloride and sodium-chloride particles impacted on a silicone-greased polycarbonate filter did not react with SO_2. Sodium-chloride and ammonium-nitrate particles impacted on a polycarbonate filter coated with five µL of silicone oil did not react to a significant extent with HNO_3 or SO_2, respectively. Acidic sodium-bisulfite particles impacted on a greased surface reacted to a limited extent with NH_3 (i.e., they were 1.7 to 3.5% neutralized).

In a 24-hour field test employing four collocated sampling systems, the concentrations of coarse-particle nitrate-N and sulfate were determined to be 0.939 ± 0.032 $\mu g/m^3$ (± 3.4%) and 0.222 ± 0.007 $\mu g/m^3$ (± 3.3%), respectively. However, substantial percentages of the nitrate, sulfate, and ammonium (36%, 44%, and 50%, respectively) were collected on the bent-tube inlets rather than on the impaction disks.

ACKNOWLEDGMENTS

Craig D. Adams, Gary G. Guinn, and Mehdi Jalali, graduate research assistants affiliated with the Environmental Health Engineering and Science Program at the University of Kansas, conducted many of the laboratory experiments. Russell W. Wiener and Robert K. Stevens of the U.S. EPA provided helpful comments and insights during the course of the study. Ed Clark skillfully machined the TFE sleeves and recessed impaction disks. Funds to support graduate research assistants and to purchase supplies and equipment were generously provided by the Civil Engineering Department, the School of Engineering, and the University of Kansas Center for Research, Inc.

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SECTION 1

INTRODUCTION

Despite the major public attention that has been focused on the problem of "acid rain", it has been recognized by scientists for some time now that a substantial fraction of the acid is actually deposited during dry weather due to the interaction of gases and aerosols with plant surfaces and the ground. So that reliable estimates of the loads of nitrogen and sulfur associated with this dry deposition can be made, scientists at the U.S. EPA and elsewhere have been working to develop quantitative methods to sample and analyze the major nitrogen- and sulfur-containing species present in gaseous and aerosol form in ambient air. These include nitric acid, nitrous acid, nitrous oxide, nitrogen dioxide, nitrate, nitrite, ammonia, sulfur dioxide, sulfuric acid, sulfate, and sulfite.

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Progress in developing sampling methods for dry deposition has been hampered by the chemical complexity of the system; several of the chemical species of interest are quite reactive and there are interactions between the solid, liquid, and gaseous components. As a result, a considerable number of artifacts have been encountered (Tanner, 1989), including: 1) adsorption of gaseous species (e.g., HNO_3 and SO_2) on the filter media or the sampling device used to collect aerosols (e.g., Spicer and Schumacher, 1977 & 1979; Klockow *et al.*, 1979; Appel, 1979, 1980, & 1984); 2) adsorption of HNO_3 and other gaseous species by particles deposited on the filter media (e.g., Klockow *et al.*, 1979; Forrest *et al.*, 1982; Appel, 1984); 3) volatilization of particulate species such as NH_4NO_3 and NH_4Cl (e.g., Forrest *et al.*, 1979 & 1982; Appel *et al.*, 1981 & 1984; Larson and Taylor, 1983; Richardson and Hightower, 1987; Hightower and Richardson, 1988); 4) reactions of species such as NO, NO_2, and PAN with components of the sampling device (e.g., Perrino *et al.*, 1988); and 5) formation and subsequent volatilization of HNO_3 as a result of metathetical or displacement reactions (e.g., Appel and Tokiwa, 1981; Anlauf *et al.*, 1986; Sturges and Harrison, 1988). A number of investigators have been working to develop sampling devices and procedures able to circumvent these problems.

One of the most significant breakthroughs in this regard was the development by Possanzini *et al.* (1983) of the annular denuder, a great improvement over the single-tube denuder used by Ferm (1979) to sample atmospheric ammonia without interference by particles. Using two annular denuders in series, most (about 99%) of the gaseous acids and bases in an air sample can be absorbed at a relatively high rate of flow. Due to the laminar flow conditions and the very short residence time in the denuder, fine particles pass through the denuder without being collected on the denuder surface and without undergoing chemical transformation.

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Since the annular denuder removes virtually all of the gaseous constituents of interest, unlike the transition flow reactor described by Durham et al. (1986), and since it does not alter the concentration or chemical composition of the fine aerosols, it is ideally suited for pretreating the airstream prior to filtration, thereby eliminating some of the aforementioned artifacts. The artifacts associated with volatilization of HNO_3 and NH_4 from the particles can be overcome by adsorbing volatilized HNO_3 and NH_4 on chemically treated backup filters (Appel et al., 1980; Anlauf et al., 1986). Sickles et al. (1986) and Vossler et al. (1988) have demonstrated the effectiveness of an annular-denuder/filter-pack sampling system for collecting gaseous and fine-particle nitrogen- and sulfur-containing species in such a way that their concentrations in the ambient air can be accurately determined.

The coarse-particle fraction, however, poses some very significant sampling and analytical problems. In general, large particles (i.e., those having an aerodynamic diameter greater than 2.5 µm) must be removed from the air stream prior to its entry into the annular-denuder filter-pack sampling system. Depending on the configuration of the sampling inlet, the large particles may fail to enter the sampling device; and those that do enter may adhere to the sampling inlet, bounce into the denuder, or pass through to the back-up filter along with the fine particles. The latter possibility is particularly worrisome from a chemical standpoint, since the large particle fraction is likely to be alkaline, while the fine particle fraction is generally acidic.

Initial attempts to circumvent the problems associated with large particles have focused on the use of either a Teflon-coated glass impactor or a Teflon cyclone to remove large particles ahead of the denuder tube (e.g., Stevens et al., 1986; Stevens, 1986; Vossler et al., 1988). However, there are potential problems with each of these devices, including: 1) particle resuspension or bounce; 2) volatilization of constituents of interest from the surfaces of large particles; and 3) reactions of gaseous constituents with trapped particles or with any grease or oil used to trap the particles. Furthermore, neither device is inherently well suited to gravimetric or chemical analysis of the large particle fraction, which would be highly desirable in view of the potential significance of the large particle fraction. Although particulate sulfate is primarily associated with fine particles, large particles can be very significant in terms of total particle mass, particulate nitrate, and particulate ammonium (e.g., Noll and Pilat, 1971; Wolff, 1984; Coe and Lindberg, 1987; Cadle and Mulawa, 1988; Wall et al., 1988; Butler, 1988 & 1989).

The objective of th~~is~~e research investigation was to develop a sampling procedure for large aerosols that would: 1) permit accurate determination of the mass and chemical composition of large particles present in ambient air over a 24-hour period; 2) employ a device that could be used in conjunction with an annular denuder and filter pack without interference in the determination of the gaseous and fine-particle constituents; 3) avoid the formation of chemical artifacts; and 4) be simple enough to deploy in a nationwide monitoring network.

SECTION 2

CONCLUSIONS

1. The cut point of the modified impactor operating at 12.5 Lpm and using a polycarbonate filter coated with 5 µL of silicone oil was experimentally determined to be 2.5 µm (aerodynamic equivalent), identical to its theoretical cut point.

2. Non-isoaxial sampling of 8-µm particles resulted in a substantial reduction in sampling efficiency, with less than 10% of the particles entering an inlet orthogonal to the air stream. Hence, accurate sampling in the field will require a vane-mounted system or some other means of orienting the sampler inlet into the wind to achieve isoaxial sampling.

3. When the samplers were mounted horizontally, minus the bent-tube inlets, significant fractions (2.0-9.0%) of 8.34-µm uranine particles were collected in the impactor inlets, presumably as a result of sedimentation or turbulent diffusion.

4. Extensive particle bounce occurred when using either an uncoated TFE impaction surface or an uncoated polycarbonate filter. Examination of sodium-chloride particles collected on an uncoated polycarbonate filter revealed that particles adhered only to the area of the filter underlain by the small dab of silicone grease used to hold the filter in place. Hence, oil or grease must be used to prevent particle bounce.

5. When using a silicone-greased impaction surface, significant particle bounce was detected at a uranine-particle mass loading of only 38 µg, representing about 70% of a monolayer for the 3.7-mm area actually impacted by particles. Hence, use of silicone grease will limit mass loadings to very low levels, precluding gravimetric analysis, unless a rotating surface or other means of reducing the mass of particles per unit area is incorporated into the design (the hollow inner tube of the denuder offers an unused space to mount a motor for this purpose).

6. Using a porous glass impaction surface coated with 50 µL of silicone oil, 27-29% of the particle mass bounced off the impaction surface when sampling uranine particles having an aerodynamic diameter of 7.9 µm (the mass loading was 4-5 µg, much less than a monolayer). Saturating the porous glass surface with mineral oil reduced particle bounce to approximately 2% of the particle mass sampled. Under severe mass loading conditions (126-2,920 µg), only about 1% bounce was observed using a polycarbonate filter coated with only 5 µL of silicone oil.

7. Since excessive bounce occurred with uncoated, greased, or lightly oiled impaction surfaces, and since the oil tended to flow sideways off oil-saturated porous glass impactions disks when the sampling system was horizontally mounted, it was determined that isoaxial sampling could best be accomplished using a vertically mounted sampling system coupled to a bent-tube inlet.

8. Inlet losses ranged from 91 to 96% for 26.5-µm uranine particles sampled using sharp-edged 90° bent-tube inlets, 48-52% for 15.2-µm ammonium-sulfate particles sampled using bent-tube inlets constructed from thin-walled glass tubing, 7-14% for 8-µm uranine particles sampled using blunt 90° bent-tube inlets, 3.7-9.5% for 7.9-µm uranine particles sampled using sharp-edged 90° bent-tube inlets mounted in an inverted position, and 0.5-5.3% (averaging 2.7%) for 7.9-µm uranine particles sampled using sharp-edged 90° bent-tube inlets mounted in an upright position.

9. When using an oiled porous glass impaction surface to collect 7.9-µm uranine particles, at least 12-15% of the total particle mass sampled became entrapped within the pores and was not readily extractable for subsequent chemical analysis. In an experiment with 8-µm ammonium-sulfate particles, recovery from an oiled porous disk was 20% lower than for the control samples, but the difference was not statistically significant under the conditions of the test. On the other hand, uranine particles collected on oiled membrane filters were readily extracted.

10. Deposition of 7.9-µm uranine particles collected on a polycarbonate filter coated with 5 µL of silicone oil indicated the presence of a double-vortexing flow condition, presumably resulting from the use of the bent-tube inlet. The particle collection characteristics of the impactor do not appear to be adversely affected by this condition.

11. Solid particle losses in the combined impactor-denuder system (exclusive of the inlet losses) were found to occur predominantly with particles about the size of the impactor's cut-point diameter. Within the denuder, losses of particles having an aerodynamic diameter of 2.0-2.8 µm ranged from 4-8% of the total mass sampled. Particles were also lost on the TFE spacer between the impactor and the denuder, representing 10-17% of the mass sampled for 2.0-2.8 µm particles. Losses of particles having other aerodynamic diameters were negligible, i.e., larger and smaller particles were collected primarily on the impaction disk and the back-up filter, respectively.

12. Analysis of four greases (Vaseline, Dow Corning high-vacuum silicone grease, Halocarbon 25-5S, and Fluorolube GR-290) and three oils (a silicone oil and two mineral oils) revealed that they were of suitable purity and were compatible with analysis of trace concentrations of anions by ion chromatography after extraction with pentane and water. They did not generally leach or sorb significant amounts of the anions of interest. The mineral oils were found to contain detectable amounts of extractable sulfate, but not enough to be significant when a small quantity of oil (less than 0.1 mL) is used in a 24-hour test. The Halocarbon grease contained a small amount of chloride and disrupted the

baseline during the early portion of the chromatograph, but did not interfere with analysis of nitrate or sulfate.

13. Silicone oil and Vaseline appeared to be compatible with gravimetric analysis of impacted particle mass. However, gravimetric analysis would only be useful for high mass loadings (i.e., those for which weighing would give reasonably accurate results), a dust-free weighing room might be needed, and additional testing is needed to determine how long the samples must be equilibrated prior to weighing.

14. Polycarbonate filters were found to be free of nitrate, nitrite, and sulfate; but mixed-fiber (cellulose acetate / cellulose nitrate) filters contained measurable amounts of leachable nitrate.

15. Silicone oil, polycarbonate filters, and Vaseline exposed to HNO_3 and SO_2 were found to sorb little if any nitrate or sulfate. The traces of nitrate and sulfate which were often detected in exposed specimens may very well have been due to handling rather than to chemical artifact formation; and the amounts detected would generally not be significant for samples collected over a 24-hour period.

16. TFE impaction disks may adsorb HNO_3 (the results were somewhat erratic); but it is not necessary to analyze the TFE disk when it is overlain by a polycarbonate filter.

17. Ammonium-chloride and ammonium-nitrate particles impacted on uncoated polycarbonate filters did not volatilize (0-1% loss) from the collection surface when exposed to purified air at a nominal flowrate of 16.7 Lpm for four hours.

18. Ammonium-chloride and sodium-chloride particles impacted on a silicone-greased polycarbonate filter did not react with SO_2.

19. Sodium-chloride and ammonium-nitrate particles impacted on a polycarbonate filter coated with 5 µL of silicone oil did not react to a significant extent with HNO_3 or SO_2, respectively.

20. Acidic sodium-bisulfate particles impacted on a silicone-greased polycarbonate filter reacted to a limited extent with NH_3 (the particles were 1.7 to 3.5% neutralized, as estimated from the increase in their ammonium ion content).

21. In a 24-hour field test employing four collocated sampling systems incorporating the modified impactors, the concentrations of coarse-particle nitrate-N and sulfate were determined to be 0.939 ± 0.032 µg/m^3 (± 3.4%) and 0.222 ± 0.007 µg/m^3 (± 3.3%), respectively. However, substantial percentages of the nitrate, sulfate, and ammonium (36%, 44%, and 50%, respectively) were collected on the bent-tube inlets rather than the impaction disks.

SECTION 3

RECOMMENDATIONS

1. Impactors used to sample large nitrogen- and sulfur-bearing particles (or to prevent their entry into downstream denuders and filter packs) should have their impaction surfaces coated with a suitable oil or grease to prevent bounce. Grease or a thin film of oil should only be used under low mass loading conditions. At higher mass loadings, excess oil should be used.

2. If an oiled porous glass disk is used as an impaction surface to collect particles for subsequent chemical analysis, the analyst should make sure that the extraction procedure used to remove the particles from the disk is adequate. If not, the extraction procedure should be modified or an oiled membrane filter should be used instead.

3. The nature of the nitrate and sulfate collected on the impactor inlet during collection of field samples should be investigated, and experiments should be conducted to ascertain whether large particles deposited in the inlet will react to a significant extent with HNO_3, SO_2, NH_3, or other gaseous pollutants.

4. A small vane system able to turn a bent-tube inlet mounted on a rotary union and orient it into the wind should be developed and field tested.

5. The efficiency with which both anions and cations associated with various types of particles can be extracted from oils and greases into water should be thoroughly examined and documented.

6. The procedure proposed herein for gravimetric determination of large particles should be perfected and field tested.

7. The reactivity of gases (not only HNO_3, SO_2, and NH_3, but also O_3, NO, NO_2, PAN, and especially SO_3) with oils and greases, with various types of Teflon and Teflon coatings, with various types of particles (especially acidic and basic particles) collected on oiled and greased surfaces, and with denuders and their coatings should be explored in much more detail than was possible in this study. The effects of temperature and relative humidity on such reactions also need to be thoroughly examined.

8. Additional field tests should be conducted to determine the precision of the procedure (described herein) under a variety of ambient conditions

and to explore ways to improve the precision and to simplify the procedure for use by individuals with minimal experience.

9. Research should continue toward the development of a sampling system capable of quantitatively sampling very large (i.e., 15-20 μm) particles without inlet losses.

10. The sampling system herein described should be thoroughly examined vis-a-vis its potential use in sampling acid aerosols. Particular attention should be given to: interactions between gases and impacted particles (see recommendation 7); procedures for quantifying the acidity or basicity of impacted particles; and loss or alteration of submicron particles as they pass through the denuders.

SECTION 4

EXPERIMENTAL APPROACH

The investigation began with a careful assessment of the advantages and disadvantages of various devices able to collect large particles and suitable for use in conjunction with the annular-denuder filter-pack system. Among the devices considered were single- and double-jet Teflon-coated glass impactors, Teflon or Teflon-coated cyclones, and modified dichotomous samplers. A PTFE/FEP-coated single-jet glass impactor, modified to facilitate gravimetric and chemical analysis of the particles captured on the impaction surface, was selected on the basis of its simplicity, low cost, and liklihood of success in meeting the stated objectives. The modified device was very similar to the Teflon-coated glass impactor used by Vossler et al. (1988), but a removable TFE disk mounted on the end of the denuder tube was used as the impaction surface, as shown in Figure 1. This design was conceived by the authors in 1986 and a prototype was designed and constructed (in cooperation with University Research Glassware, Carrboro, NC) as part of another project previously funded by the U.S. EPA (Grant R812280-01-0). This design was subsequently incorporated into sampling systems used by other investigators (e.g., Koutrakis et al., 1988a & 1988b; Stevens et al., 1988a & 1988b).

The removable TFE impaction disk (Figure 1) can be used uncoated to capture wet or "sticky" particles; or it can be coated with grease, covered with an oil-saturated filter, or fitted with an oil-saturated or lightly oiled porous (fritted) glass disk to reduce particle bounce. The disk was designed similarly to those used for scanning electron microscopy (SEM) with the intention of eventually extending its application to many other types of particles, especially those for which SEM analysis might offer a distinct analytical advantage.

The use of an oil-saturated impaction surface dictates a vertical impactor orientation (to prevent oil from dripping off), whereas the use of grease or a thin film of oil allows either a vertical or a horizontal orientation to be used. In the latter case, particle bounce may occur at high mass loadings, i.e., those that produce more than one layer of particles. Since ambient wind directions are generally horizontal or nearly so, non-isoaxial sampling conditions will exist when the impactor is used in the vertical position. Under these sampling conditions, one of the resulting effects that becomes of interest is the elutriation of particles as the flow stream passes over the straight impactor inlet. An inlet with a 90° bend can be used with a vertically positioned impactor to sample isoaxially and thus eliminate the elutriation effect, but the inlet bend presents an additional surface where particle deposition and chemical artifact formation may occur.

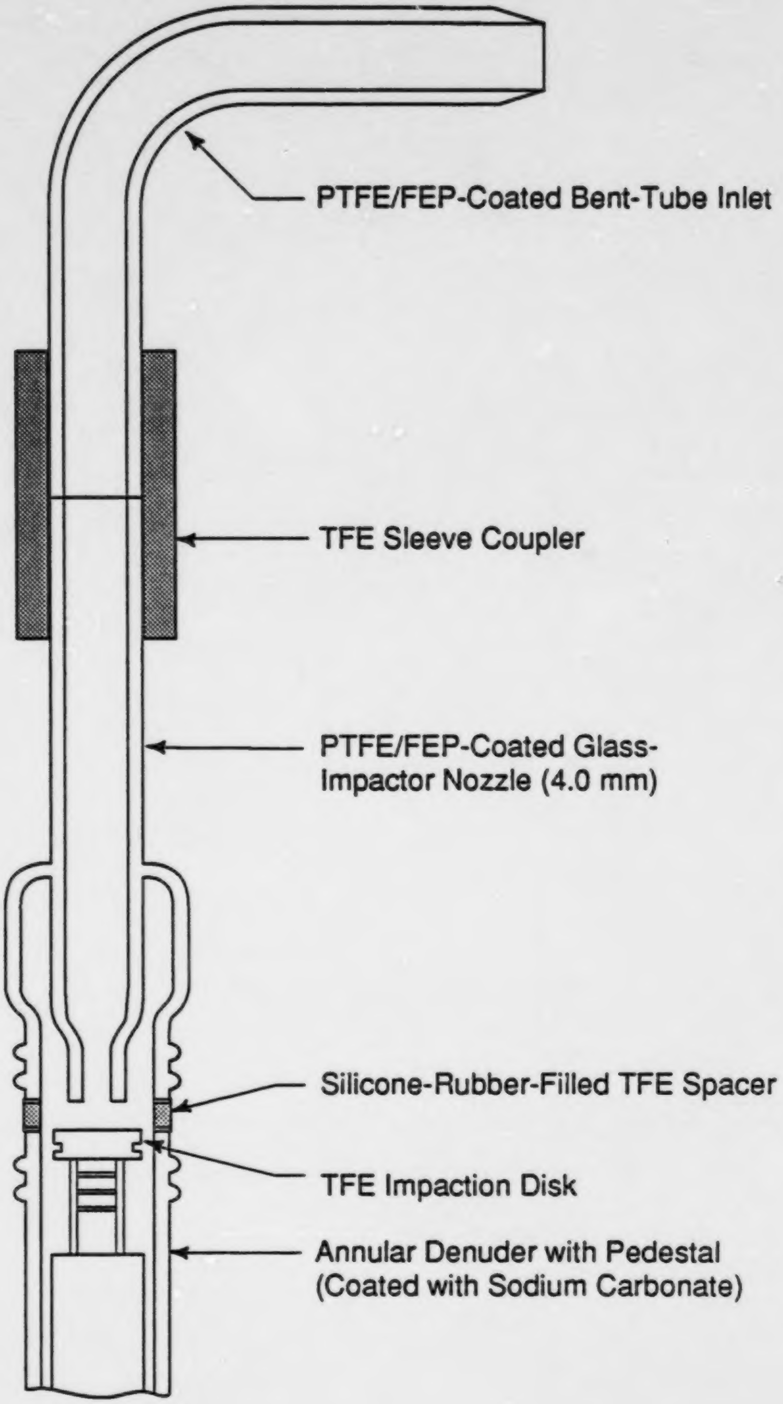
PTFE/FEP-Coated Bent-Tube Inlet
TFE Sleeve Coupler
PTFE/FEP-Coated Glass-
Impactor Nozzle (4.0 mm)
Silicone-Rubber-Filled TFE Spacer
TFE Impaction Disk
Annular Denuder with Pedestal
(Coated with Sodium Carbonate)

Figure 1. Modified PTFE/FEP-coated glass impactor with bent-tube inlet.

To avoid both the effects of elutriation and bent-tube inlet losses that could occur with a vertically oriented system, the impactor could be operated horizontally, i.e., isoaxially, using grease or a thin film of oil to coat the impaction surface. However, larger particles may still settle out in the inlet. In addition, there is a limit to the particle load that can be collected on a greased or lightly oiled impaction surface, especially over a 24-hour sampling period. Thus, regardless of which impaction surface coating is used to reduce particle bounce, its influence on the orientation, performance, and operation of the sampling system must be considered.

To gain insight into certain aspects of the impactor's performance and operational characteristics, experiments were conducted to examine: 1) the cut-point of the modified impactor; 2) particle collection efficiency under non-isoaxial sampling conditions; 3) inlet losses as a function of particle size; and 4) particle bounce as a function of mass loading using different coatings in varying amounts. These experiments examining the physical aspects of the impactor were not intended to provide a comprehensive solution to the age-old large-particle sampling problem. Rather, they were intended to characterize the physical performance (and limitations) of the impactor, to aid in the conduct and interpretation of subsequent experiments addressing chemical artifact formation, to reveal problems requiring further investigation, and most of all to determine the size of particles that could be successfully sampled.

Selected oils and greases that might be used to prevent particle bounce were examined, and experiments were conducted on the most promising candidates to determine: 1) their purity; 2) their compatibility with analysis of trace anions by ion chromatography; 3) their gravimetric stability; 4) their ability to react with gaseous constituents to form chemical artifacts; and 5) their ability to prevent reactions that might occur between reactive gasses and impacted particles.

Based on the results of the laboratory experiments, the most promising sampling system was tested in the field using a 24-hour sampling period. The use of four collocated sampling systems permitted a determination of the overall precision of the entire procedure for the concentrations of constituents present on the day the samples were collected.

SECTION 5

MATERIALS

A. SAMPLING SYSTEM COMPONENTS

The sampling system consisted of the modified impactor (shown in Figure 1) coupled to the annular-denuder filter-pack assembly described by Vossler et al. (1988). A complete two-denuder sampling system is shown in Figure 2.

The PTFE/FEP-coated glass bent-tube inlet was designed similarly to the sampling tip specified by ASTM (1986) for particle sampling (method D3685-78), with an ID of 1.1 cm, each leg approximately 6-7 cm long, and a sharp-edged tip. The inlets were fabricated by University Research Glassware (Carrboro, NC) to match the impactors made by the same company. Each inlet was semi-permanently attached to an impactor using a tight-fitting 2.2-cm-OD TFE sleeve and TFE pipe-thread tape. A few preliminary experiments were conducted using either "home-made" bent-tube inlets constructed from 1-cm-ID thin-walled glass tubing or blunt-tipped bent-tube inlets designed by University Research Glassware to slip over an impactor nozzle and to be attached by means of a compression fitting.

Single-jet PTFE/FEP-coated glass inertial impactor nozzles (see Figure 1), designed using the recommendations of Marple and Rubow (1986) to have a cut-point of 2.5 μm (aerodynamic diameter), were purchased from University Research Glassware. Each nozzle was checked with a micrometer to be sure its jet diameter was 4.00 ± 0.05 mm. The nozzles were of three types: 1) an older style nozzle having a relatively abrupt (ca. 30°) transition from the inlet to the jet; 2) a newer style nozzle having a more tapered inlet to jet transition (ca. 10°); and 3) an "unbreakable" PTFE/FEP-coated aluminum nozzle having a removable TFE jet (4.0 mm).

The impactor nozzles were connected to denuder tubes having pedestals for mounting the impaction disks (Figure 1). These connections were made using threaded butt-joint couplers and TFE spacers having a synthetic silicone-rubber core. Two types of TFE spacers were used: unattached spacers and spacers integrally built into the couplers. Both types were obtained from University Research Glassware and both had a thickness of about 6 mm, giving a jet-to-plate-distance to jet-diameter ratio of about 1.5.

Several types of impaction disks having the same basic shape and dimensions were used. The impaction disk most heavily (and most successfully) used was machined from virgin TFE and featured a small (77-μL) "well" 14 mm wide and 0.5 mm deep, as shown in Figure 3. This well was designed to accept either a small pool of oil (underlain by a 13-mm polycarbonate membrane

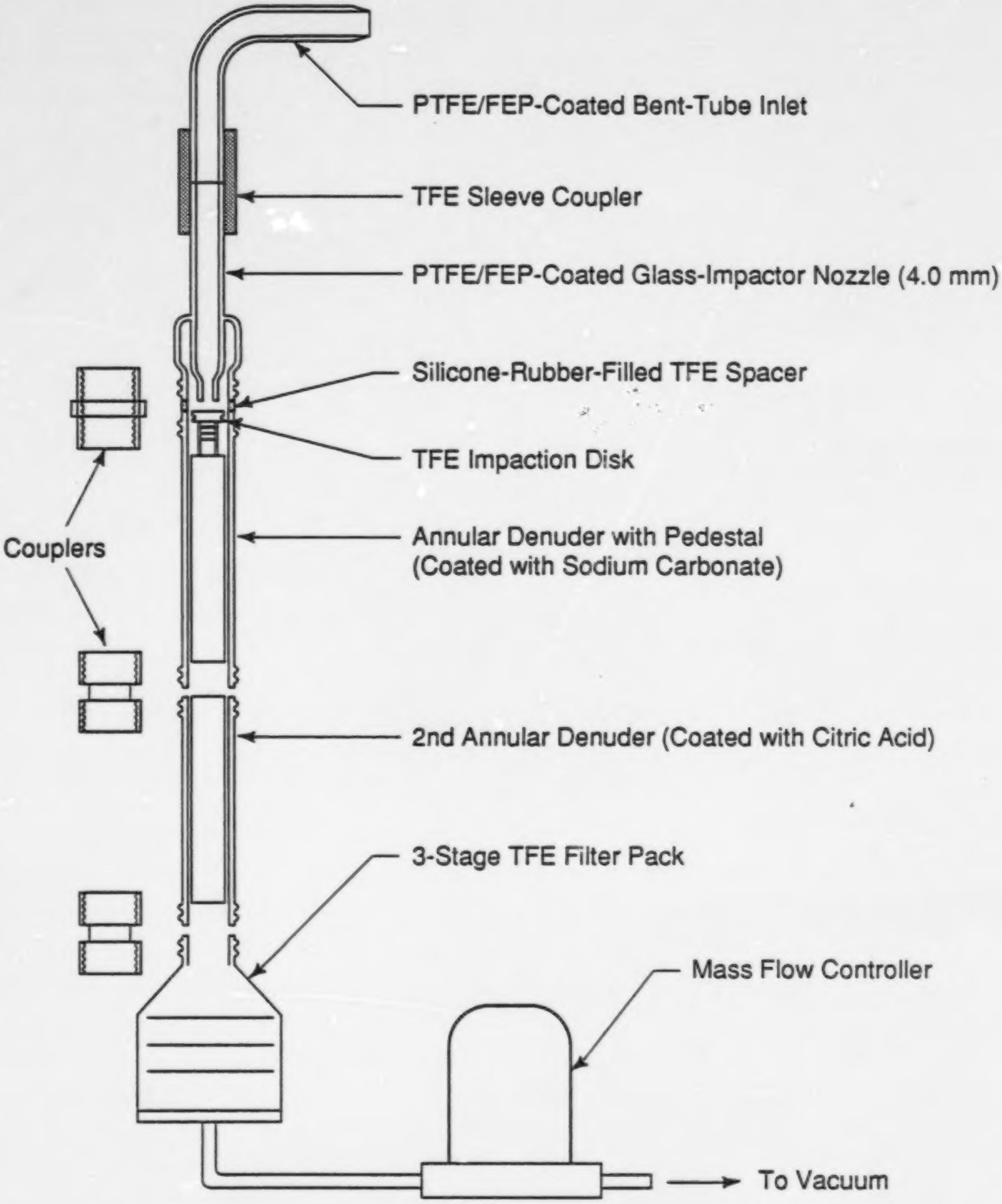
PTFE/FEP-Coated Bent-Tube Inlet
TFE Sleeve Coupler
PTFE/FEP-Coated Glass-Impactor Nozzle (4.0 mm)
Silicone-Rubber-Filled TFE Spacer
TFE Impaction Disk
Couplers
Annular Denuder with Pedestal (Coated with Sodium Carbonate)
2nd Annular Denuder (Coated with Citric Acid)
3-Stage TFE Filter Pack
Mass Flow Controller
To Vacuum

Figure 2. Glass-impactor annular-denuder filter-pack sampling system.

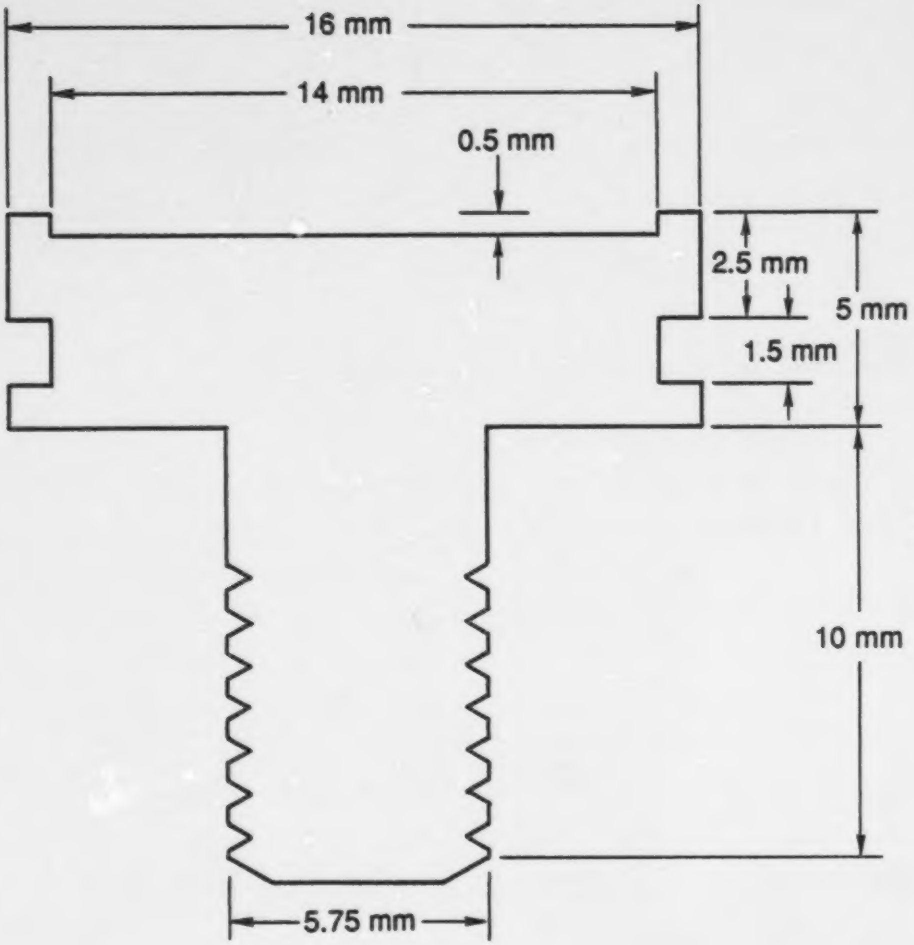
16 mm
14 mm
0.5 mm
2.5 mm
5 mm
1.5 mm
10 mm
5.75 mm

Figure 3. TFE impaction disk with well.

filter) or an oiled or greased 13-mm membrane or glass-fiber filter. It wasmost frequently used with a silicone-oiled polycarbonate (Nuclepore) filter, which was found to migrate if placed on flat impaction surface (i.e., an impaction disk without a well).

A variety of filter materials were considered for use with the impaction disk, including polycarbonate, PTFE, and mixed-fiber (cellulose acetate and cellulose nitrate) filters. Nylon and glass fiber filters were not considered due to their well known reactivity with nitric and sulfuric acid vapors. The mixed-fiber filters were used in several tests, but yielded high nitrate blanks, as expected. (Prewashing could lower the blank values but would unnecessarily complicate the procedure.) Both polycarbonate and PTFE filters were considered because of their resistance to adsorption of SO_2 and HNO_3 (Klockow et al., 1979; Spicer and Schumacher, 1979; Appel, 1979 & 1984; Anlauf et al., 1986); but polycarbonate filters were selected over PTFE filters because of the lower blank values they gave for sulfate and because of their superior compatibility with SEM analysis. A 0.4-µm pore size was selected under the assumption that large particles (>2.5 µm) would be unable to penetrate into the pores. Polycarbonate (Nuclepore) filters having a smaller pore size (0.015 µm) were tried, but silicone oil would not satisfactorily wick up on them.

Several other types of impaction disks, each made from TFE and having the same basic "SEM-pin" shape, were also fabricated or purchased:

1) "plain" disks having a flat 16-mm top (these disks satisfactorily supported greased membrane filters; but oiled membrane filters placed on them moved under the force of the jet, so they were abandoned in favor of the design shown in Figure 3);

2) disks very similar to those shown in Figure 3 but having a 50-µL well 10 mm in diameter and 0.64 mm deep (these disks were intended to be used only with oil or oiled 10-mm filters, but without a filter the oil could not be retained under the force of the jet; and it was decided to switch to the design shown in Figure 3 when using filters, since the larger diameter well would be less likely to alter the cut point);

3) disks having a well 10 mm in diameter and 3.5 mm deep, deep enough to accept a fine-pore (4-5.5 µm) 3-mm-thick fritted glass disk (Porosity E, Ace Glass, Vinland, NJ) and to leave 0.5 mm (i.e., 50-µL volume) between the top of the glass disk and the top of the impaction disk (these disks were used only for collecting field samples as part of another project; they permitted use of an oil-saturated sintered metal or porous-glass disk while minimizing the potential for loss of oil and, by virtue of the fine pores, minimized the liklihood that impacted particles would become entrapped in the pores of the glass disk); and

4) disks fitted with a coarse 10-mm fritted (porous) glass disk flush with or slightly protruding from the top of the impaction disk. Some of these disks had three holes drilled through their top (head)

sections to permit removal of the glass disk using a special tool. Both the disks and the tool were supplied by University Research Glassware.

Except where otherwise noted, the disks used were those described in Figure 3; and the porous glass disks used were those described in item 4 above.

Denuders (with and without pedestals), two-stage filter packs, and various caps and connectors, all as described by Vossler et al. (1988), were obtained from University Research Glassware. The denuders had a 28-mm OD and a 1-mm annular space; those with a pedestal for mounting an impaction disk were 26.5 cm long and those without pedestals were 24.2 cm long. The filter packs were constructed of virgin TFE, with stainless-steel support plates and an aluminum base.

B. OILS AND GREASES

Four greases and three oils were selected for study. The greases were: 1) petroleum jelly (Vaseline, Chesebrough-Pond's Inc., Greenwich, CT); 2) high-vacuum silicone grease (Dow Corning Corp., Midland, MI); 3) Halocarbon grease, type 25-5S (Halocarbon Products Corp., Hackensack, NJ); and 4) Fluorolube grease, type GR-290 (Hooker Chemical Co., supplied by Fisher Scientific Co., Fair Lawn, NJ).

The oils used were: 1) silicone diffusion-pump oil (type 704, Dow Corning, Midland, MI); 2) a mineral oil (Fisherbrand 19 mechanical pump fluid) distributed by Fisher Scientific Co. (Pittsburgh, PA); and 3) a mineral oil (Duo Seal pump oil) supplied by Sargent-Welch Scientific Co. (Skokie, IL).

C. CHEMICAL REAGENTS

All chemicals used were ACS reagent grade or better. Without exception, the water used for preparation of samples and reagents was Milli-Q reagent-grade water (Millipore Corp., Bedford, MA) meeting or exceeding the ASTM specifications for Type I reagent water and containing no detectable quantity of any analyte of interest, except for an occasional trace of chloride that most likely resulted from sample handling.

SECTION 6

ANALYTICAL METHODS

A. INORGANIC ANIONS

Chloride, bromide, nitrite, nitrate, phosphate, and sulfate were determined using a Dionex Model 2000i Ion Chromatograph (Dionex Corp., Sunnyvale, CA) equipped with an IonPac AS4A separation column, an IonPac AG4A guard column, and an automated sampler. The methodology was similar to that described by O'Dell et al. (1984), except that:

1) a bromide standard (1.4894 gms KBr per liter) was often included and the fluoride standard was usually deleted;

2) the nitrite, nitrate, and phosphate stock standards were preserved using chloroform (1 mL/L);

3) fresh stock standards were prepared annually and fresh working standards were prepared monthly, the longer storage times having been justified by comparisons between aged and fresh standards;

4) samples potentially containing sulfite were treated with one or two drops of 3.0% hydrogen peroxide to oxidize sulfite to sulfate;

5) all samples and standards were dosed (100 µL per 10 mL) with a concentrated (110-fold-strength) eluant solution to eliminate the "water dip" from the chromatograms so that the early eluting peaks could be more easily and more accurately integrated;

6) a different eluant (2.3 mM sodium carbonate plus 1.3 mM sodium bicarbonate) was used to sharpen the sulfate peak (RT≈6.0 minutes) while maintaining good peak separation; and

7) the 5-mL autosampler vials and filter caps were soaked in 0.1 M sodium bicarbonate, thoroughly rinsed with reagent water, dried, and stored in clean ziplock bags.

The chromatographic peaks were integrated using a Spectra-Physics Model 4270 integrator (Spectra-Physics, San Jose, CA) with the settings optimized for detection and accurate quantification of small peaks. Standards having concentrations of 20, 50, 100, 200, 500, 1000, 2000, 5000, 7000, and 10000 µg/L were routinely used to calibrate the instrument. Calibration "curves" (regression equations) were prepared by dividing the standards into two groups (20-500 µg/L and 500-10,000 µg/L), and using a spreadsheet (Supercalc 4, Computer Associates International, San Jose, CA) on a personal computer (Z159, Zenith Data Systems Corp., St. Joseph, MI) to fit the data using a quadratic least-squares regression routine.

The low-range standard curves were very linear, with intercepts close to the origin. The high-range standard curves were sometimes slightly curvilinear (concave upwards) at high concentrations, such that a quadratic regression fit the data much better than a linear regression. When multiple injections of each standard were made, outliers identified using Grubb's test (Rohlf and Sokal, 1981) were discarded. The results for a typical calibration run are shown in Table 1. Samples having analytes higher in concentration that the highest standard included in the regression were diluted and analyzed again.

Instrument response was very constant over time, as demonstrated by the results in Table 2. These results are rather remarkable considering the fact that the data were obtained using four different eluant formulations, two different detectors, two different sets of columns, and four different sets of freshly prepared working standards. As a result of the constant instrument response, it was possible to merely check the calibration on a daily basis and to calibrate the instrument monthly using multiple (8-10) injections of each standard to achieve a very accurate calibration.

The accuracy of the IC analysis was occasionally checked by analyzing external quality-control samples obtained from the U. S. EPA Environmental Monitoring and Support Laboratory in Cincinnati, OH. The measured values for fluoride, chloride, nitrate, phosphate, and sulfate (in the mineral, nutrient, and nitrate/fluoride samples) were within 6% of the stated value except for two of the fluoride samples having concentrations below 1 mg/L.

Accuracy was also assured by checking old stock and working standards against fresh standards. Stock nitrite, nitrate, and phosphate standards stored for more than one year did not differ from fresh stock standards. Working standards stored for up to six months were also found to be stable (see Table 3), but fresh working standards were always used for instrument calibration.

Analytical precision was generally better than ± 2% at concentrations above 1,000 µg/L, in good agreement with Stevens et al. (1988a & 1988b). At lower concentrations, precision was a function of both concentration and the sensitivity of the detector for the analyte of interest. The results shown in Table 4 are typical of those obtained on a number of occasions, except that the precision for the 1,000 µg/L standard was unusually poor. At high concentrations (above 1,000 µg/L) much of the variance was attributed to imprecision in the functioning of the autosampler and sample injector, since outliers were generally associated with a particular injection and since the precision at higher concentrations was generally not analyte dependent. Individual outliers occurred rarely and could usually be attributed to the response of the integrator to baseline noise.

TABLE 1. RESULTS OF A TYPICAL IC CALIBRATION RUN (9-24-88)*

Actual Concentration, µg/L	Calculated Concentration, µg/L				
	Cl	NO_2-N	PO_4-P	NO_3-N	SO_4
20	19	20	21	20	21
50	56	50	49	50	49
100	94	100	100	100	99
200	202	200	200	200	201
500	500	500	500	500	500
1000	1029	982	992	982	990
2000	1968	1997	1990	1988	2010
5000	4948	4999	4984	5005	4996
7000	7065	6411†	7018	6998	6994
10000	9981	7559†	9995	9671†	10002
Regression of Low-Range Standards					
Quad. regr. constants					
a	.0003189	-.000032	-.000147	-.000021	-.000165
b	1.199257	.6117572	1.518064	.5451903	1.838223
c	-4.65363	.7174788	.8212824	.7696359	-1.70119
Corr. coefficients:					
Linear	.9997499	.9999995	.9999941	.9999998	.9999856
Quadratic	.9995151	.9999398	.9999624	.9999602	.9999677
Range of standards used:					
Maximum	20	20	20	20	20
Mimimum	500	500	500	500	500
Regression of High-Range Standards					
Quad. regr. constants:					
a	-.000010	-.000003	-.000023	-.000003	-.000028
b	1.136330	.5370008	1.408642	.4844354	1.807858
c	161.4967	54.60830	33.60282	58.00536	-7.81234
Corr. coefficients:					
Linear	.9999204	.9999791	.9999947	.9999905	.9999960
Quadratic	.9996258	.9999064	.9991336	.9996034	.9996162
Range of standards used:					
Mimimum	1000	500	500	500	500
Maximum	10000	5000	10000	7000	10000

* Ten replicates were run for each concentration; fluoride and bromide were omitted; and the data were fit to the equation: $y = ax^2 + bx + c$.

† Excluded from the regression; this concentration saturated the detector.

TABLE 2. VARIATION IN IC RESPONSE WITH TIME

	Peak Area for a 1,000 µg/L Standard*					
Date	Cl	NO_2-N	PO_4-P	Br	NO_3-N	SO_4
06-25-88	748	1711	682	328	1895	554
07-25-88	755	1751	685	329	1911	560
07-29-88	768	1783	691	333	1937	560
08-01-88	771	1747	672	325	1894	553
08-11-88	740	1717	672	328	1911	555
09-24-88	768	1744	688	---	1934	557
Avg.	758	1742	682	329	1914	557
Std. Dev., %	1.7	1.5	1.2	0.9	1.0	0.5

* Average of 8-10 replicates.

TABLE 3. STABILITY OF WORKING STANDARDS OVER TIME

		Concentration Measured on 3-16-83*					
Date Prepared	Conc. µg/L	Cl	NO_2-N	PO_4-P	Br	NO_3-N	SO_4
09-28-87	100	128	104	104	101	102	94
	400	417	401	392	386	403	402
10-18-87	100	110	101	111	106	98	101
	400	427	396	389	401	407	420
12-07-87	400	406	400	399	380	397	404
02-04-88	20	23	22	31	21	21	22
	100	109	104	103	99	104	92
	200	211	210	196	200	213	217

* Using linear rather than quadratic regression and an old AS4 column not as sensitive for phosphate as the AS4A.

TABLE 4. Precision of IC Analyses of 9-24-88*

Conc.	Chloride		Nitrite-N		Phosphate		Nitrate-N		Sulfate	
µg/L	µg/L	%SD	µg/L	%SD	µg/L	%SD	µg/L	%SD	µg/L	%SD
20	0.84	4.2	0.33	1.6	3.50	17.5	0.81	4.1	2.18	10.9
50	1.19	2.2	0.83	1.7	5.08	10.2	1.21	2.4	3.53	7.1
100	2.11	2.1	1.36	1.4	2.65	2.7	1.60	1.6	5.84	5.8
200	3.45	1.7	3.63	1.8	5.60	2.8	3.81	1.9	6.45	3.2
500	8.04	1.6	5.40	1.1	7.49	1.5	5.78	1.2	6.56	1.3
1000	24.8	2.5	22.3	2.2	22.8	2.3	22.8	2.3	25.2	2.5
2000	33.5†	1.7†	42.7†	2.1†	25.2†	1.3†	26.1†	1.3†	21.5†	1.1†
5000	91.5	1.8	80.9	1.6	86.1	1.7	86.3	1.7	83.5	1.7
7000	117.3	1.7	49.1	0.7	111.5	1.6	95.9	1.4	89.3	1.3
10000	127.4	1.3	51.6	0.5	142.2	1.4	106.0	1.1	157.0	1.6

* Determined by injecting 10 replicates at each concentration.

† One outlier was discarded (Grubb's test, $\alpha = 0.05$, one-tailed; or if 3 or more outliers occurred for one injection, all peaks for that injection were discarded as invalid).

Blank samples were run daily to check the purity of the reagent water and the cleanliness of the vials and caps. On several occasions, a large number (12-25) of blanks were run due to suspected contamination of the 5-mL vials and caps, but all such samples were found to contain only an occasional trace of chloride. Similar tests on the 0.5-mL vial caps (which were not soaked in bicarbonate solution prior to use) revealed traces (10-20 µg/L) of chloride and sulfate. The 0.5-mL vials were used only for the field-test analyses; the caps were first rinsed with 5-10 mL of reagent water to remove any impurities associated with them, and the vials were rinsed with reagent water and then rinsed with the sample to be analyzed.

The Dionex Model 2000i ion chromatograph was put on line in March of 1988. Samples generated before that time, including some of those reported by Lane et al. (1988), were analyzed by manual injection into a Dionex QIC ion chromatograph equipped with an AS4 separation column, an AG4 guard column, and a Spectro-Physics Autolab System I integrator and a Linear chart recorder (Linear Instruments Corp., Irvine, CA).

B. AMMONIUM AND URANINE

Ammonium was determined using an Alpkem continuous flow analyzer having a detection limit of 0.01 mg/L and a precision of 0.01 mg/L at concentrations below 1.0 mg/L. Samples containing citric acid were neutralized prior to analysis.

Uranine (sodium fluorescein) was determined using a fluorometer (G.K. Turner, Model 111) equipped with a far-UV lamp (GE G4T4-1) and primary filters 2A and 47B to select an emission wavelength of 436 nm. Instrument sensitivity was adjusted by changing the intensity of the exciting light using the stepwise sensitivity range selector. By changing the position of the selector, the slit opening in front of the far-UV light source could be adjusted to provide reproducible sensitivity adjustments in increments of 1X, 3X, 10X, and 30X. The greatest sensitivity is achieved from the 30X setting, which provides the highest intensity light. The response dial has a linear scale that gives values of transmittance in 1% increments (readable to 0.5%) between 0 and 100%.

Calibration of the fluorometer was done using standard uranine solutions with concentrations ranging from 0.5 to 100 µg/L. A power-law calibration curve was developed for each sensitivity range setting. For each calibration curve, the log values of the dial readings were highly correlated ($r = 0.997$ to 1.000) with uranine concentration. At the most sensitive setting, uranine concentrations as low as 0.5 µg/L could be detected.

The concentration of uranine in each sample was calculated using the power-law calibration curve for the most sensitive setting that could be used. The power-law equation is:

$$C = a \cdot F^{b}$$

where C is the concentration of uranine in µg/L, F is percent transmittance, and a and b are constants.

Samples were obtained following each test by rinsing the respective surfaces of the impactor and denuder with reagent water. Filters or porous glass disks that had been oiled or greased were first sonified for 10 minutes in pentane before being extracted with a suitable quantity of water (5-50 mL, depending upon the concetration anticipated) using a vortex mixer and at least 10 more minutes of sonification. Back-up filters were carefully removed from the filter pack and immersed in reagent water.

The minimum amount of reagent water used to rinse any particular surface was 5 mL. The minimum amount of water used to completely immerse a 47-mm TFE back-up filter was 10 mL. These volumes established the minimum detectable mass deposited of 0.0025 µg for an impactor or denuder surface and 0.005 µg for the back-up filter. Dilution of the sample rinse volumes was often necessary, and the appropriate dilution factor was used in determining the uranine concentration. A reagent blank was used to zero the instrument and to check its stability in each sensitivity range.

SECTION 7

EXPERIMENTAL APPARATUS AND PROCEDURES

A. PARTICLE GENERATION

Particles were generated using a Berglund-Liu Monodisperse Aerosol Generator equipped with a Krypton-85 charge neutralizer. The size, shape, and uniformity of the particles were verified by scanning electron microscopy (SEM). In all cases the particles were solid and spherical.

Solid particles of a variety of types and sizes were produced by varying the concentration and composition of the solution fed to the aerosol generator. Particles spanning a size range of < 1 µm to 30 µm and particles composed of uranine (sodium fluorescein), ammonium chloride, ammonium nitrate, ammonium sulfate, sodium chloride, and sodium bisulfate were used over the course of the investigation. Actual particle diameters were determined using a scanning electron microscope; and aerodynamic diameters were computed assuming that the density of each type of particle was equivalent to that of the solid from which it was generated.

B. PREPARATION OF IMPACTION SURFACES

The impaction disks (described in Section 5A) were scrupulously cleaned prior to use. They were first wiped to remove oily deposits, then sonified in pentane to remove any remaining oil or grease, soaked in sodium bicarbonate to remove adsorbed anions, rinsed extensively in reagent water, and dried. Final preparation was done in one of the following ways:

1) Oiled membrane filters were prepared by carefully placing a clean 13-mm polycarbonate membrane filter (with 0.4-µm pores) in the well on top of the disk and then placing the desired amount of oil (most commonly 5 µL of silicone oil) on top of the filter using a digital Eppendorf micropipet (Brinkman Instruments Inc., Westbury, NY) fitted with a 100-µL polypropylene tip. The oil slowly saturated the filter, leaving a thin film on top. (A complete description of the procedure used for the field tests is included in Appendix A).

2) Uncoated polycarbonate filters (having 0.4-µm pores) were usually held in place by first adding a very small dab of silicone grease to the top of the impaction disk.

3) Greased membrane filters were prepared by placing ten 50-µL portions of a 1% solution of grease (usually silicone) in pentane on top of

the filter, allowing the solvent to evaporate after adding each 50-μL portion. (In preliminary experiments involving larger amounts of grease, it was found that a thick layer of grease would deform under the force of the jet, which could potentially alter the cut point of the impactor. Since grease does not wick up onto surfaces, a thin layer is expected to be just as effective as a thick layer, but this was not experimentally verified.)

4) Greased impaction disks were prepared as described in item 3, omitting the membrane filter. In some of the earliest experiments, a silicone-grease-saturated toluene solution was used; and in one experiment, membrane filters were placed on top of greased disks.

5) Oiled fritted glass disks were prepared in one of two ways: adding oil dropwise to saturate the disk or adding a fixed amount of oil in a pentane solution as described in item 3 above.

C. PARTICLE IMPACTION AND ANALYSIS

Particles generated in the laboratory were impacted by inserting the impactor inlet (with or without the bent-tube inlet) into either a wind tunnel or a plastic pipe into which the particles had been introduced. The wind tunnel was used for low mass loadings and the pipe was used for high mass loadings.

The characteristics of the windtunnel (shown in Figure 4) have been previously reported by Lane and Stukel (1978). The windtunnel specifications insured that the particles were completely dispersed at a uniform density before reaching the test section. Provision was also made for turbulent intensity control (< 0.7 at the test section) and accurate measurement of windtunnel free stream velocities. The 1.83-m test section was constructed of plexiglass and had a one-foot square cross-section. The capacity of the aerosol generator was such that only low mass loadings could be achieved at the desired volumetric sampling rate.

To facilitate sampling at higher mass loading rates, an alternate system consisting of an 5.0-foot length of 1.5-inch PVC pipe was constructed. The particles (still partially wet) were released into one end of the pipe, and the impactor inlet was inserted through a stopper in the other end of the pipe to draw the particles through the pipe. The pipe length was selected such that the particles would dry before reaching the impactor.

The impactor was connected to a denuder tube, which was in turn connected to a filter pack containing a back-up filter. A vacuum line connected the filter pack to a flow controller (Model 52-31T-4-888, Scott Specialty Gasses) and vacuum pump. The flowrate through the impactor was regulated, by means of a needle valve on the flow controller, to 16.7 Lpm (nominal) for some experiments and to 12.5 Lpm actual for others. Actual flowrates are reported for standard conditions of 25°C and 14.7 psi, with corrections made to account for ambient temperature and the operating pressure of the flow controller.

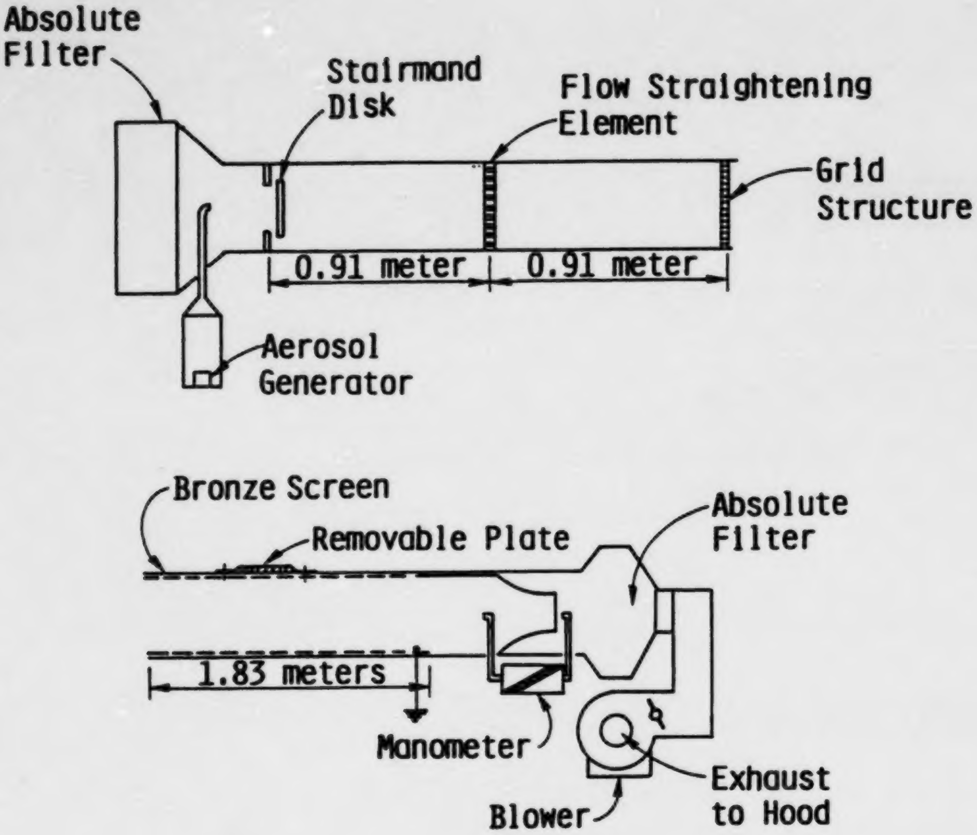
Absolute Filter
Stairmand Disk
Flow Straightening Element
Grid Structure
0.91 meter
0.91 meter
Aerosol Generator
Bronze Screen
Removable Plate
Absolute Filter
1.83 meters
Manometer
Exhaust to Hood
Blower

Figure 4. Design of the wind tunnel.

The impacted particles were either analyzed directly or used for subsequent experiments and later analyzed. Particles collected on oiled or greased Nuclepore filters were generally analyzed as described in Appendix A (extraction into pentane followed by extraction into water), but the entire impaction disk (not just the filter) was sometimes extracted. Oiled porous glass disks were analyzed in much the same way, but these were generally sonified for 5 to 10 minutes in an effort to increase removal of the impacted particles.

D. TESTS FOR CHEMICAL ARTIFACT FORMATION

Oils, greases, filters, and impacted particles were exposed to various gases (SO_2, HNO_3, NH_3, or purified air) by placing an appropriately prepared specimen into an impaction-surface exposure system (Figure 5) or an impacted-particle exposure system (Figure 6). Ambient (laboratory) air entered each system through two parallel 2.5" dia. x 11.5" air purifiers (W.A. Hammond Drierite Co., Xenia, OH) charged with equal layers of citrate-treated granular activated carbon (6-14 mesh, Fisher Scientific Co., St. Louis, MO), untreated granular activated carbon, and 4-8 mesh soda lime to adsorb NH_3, volatile organic chemicals and ozone, and acidic gases, respectively. Large scrubbers were used, rather than denuders, to permit processing of large amounts of air for extended periods of time without regeneration.

The air exiting the air purifiers was filtered through 47-mm glass-fiber filters (Whatman 934 AH), held in Nalgene in-line polycarbonate filter holders, to remove particles passing through or released from the purifier media. Immediately following the filters, a denuder tube could be inserted into the line. This denuder was generally omitted, but a citric-acid coated denuder was used for some of the experiments, especially those involving NH_3.

A side-stream of nitrogen gas, carrying the reactive gas of interest, was introduced through a stainless-steel Swagelock tee. This side-stream flow was generated by releasing compressed nitrogen, regulated to 5 psi, through a Hoke microvalve (to control the flow to about 50-60 cc/min), a 25-mm membrane filter (HAWP, Millipore Corp., Bedford, MA) held in a Delrin filter holder with 1/8" NPT fittings, and a 2- or 4-liter 3-port polypropylene reservoir (Dionex Corp., Sunnyvale, CA) filled with 1.5 or 3.5 L of solution, respectively. The nitrogen was introduced into one port and flowed over the solution to the opposite side of the reservoir. The third port was plugged. The pressure was reduced upstream of the reservoir to minimize condensation of moisture in the tubing between the reservoir and the tee; and a glass-wool plug in the tee connection provided added insurance against aerosol generation by the side stream. A solution of 0.1% nitric acid in 50% sulfuric acid was used to generate HNO_3 vapor; a solution of 0.5 mL of 30% ammonium hydroxide in 4L of 2.5N NaOH was used to generate NH_3 vapor; and a solution of 10 mL of 6% H_2SO_3 in one liter of a 50-gm/L solution of KH_2PO_4 adjusted to pH 4.8 was used to generate SO_2 vapor.

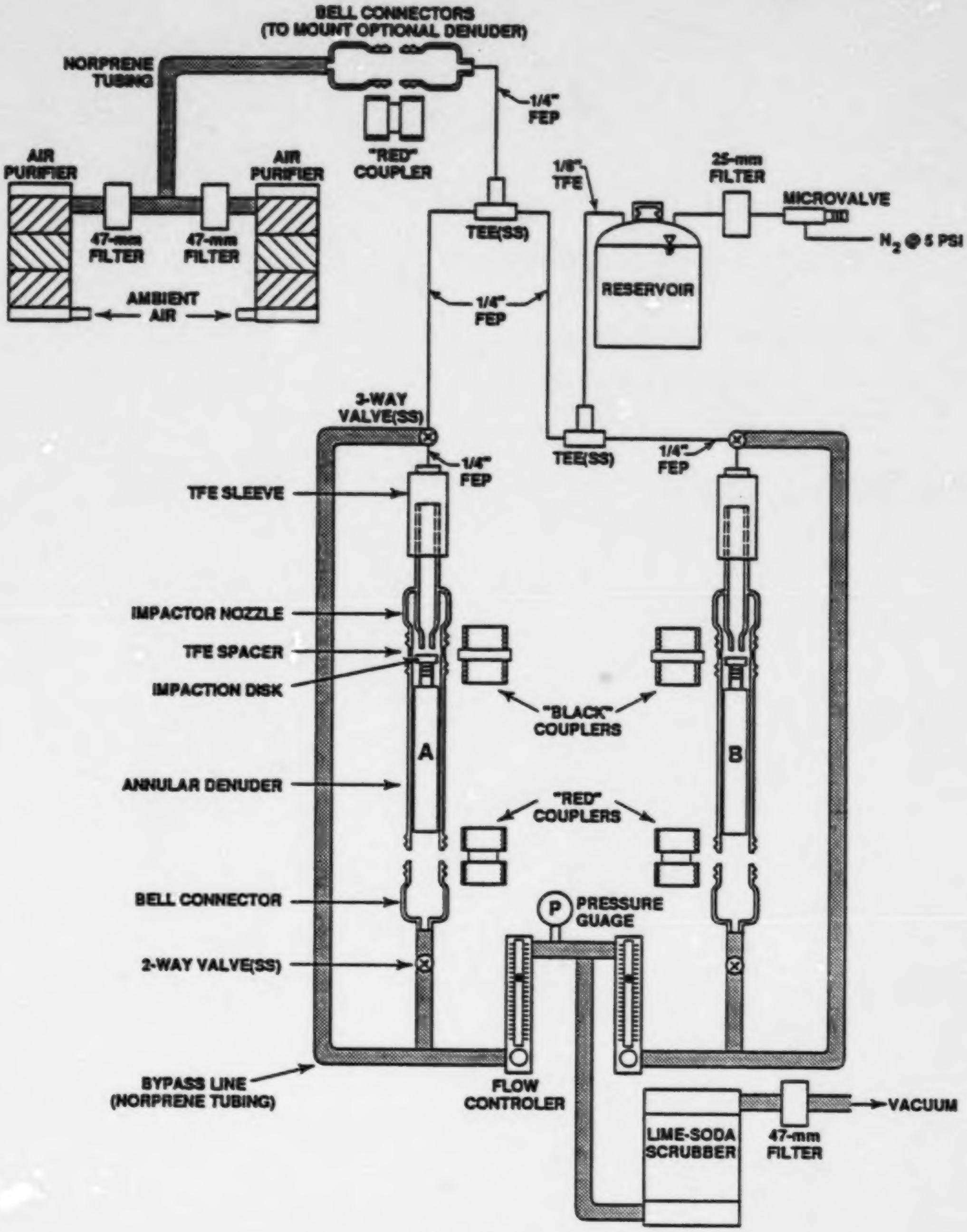
BELL CONNECTORS
(TO MOUNT OPTIONAL DENUDER)
NORPRENE TUBING
1/4" FEP
"RED" COUPLER
AIR PURIFIER
AIR PURIFIER
47-mm FILTER
47-mm FILTER
AMBIENT AIR
TEE(SS)
1/8" TFE
25-mm FILTER
MICROVALVE
N_2 @ 5 PSI
RESERVOIR
1/4" FEP
3-WAY VALVE(SS)
1/4" FEP
TEE(SS)
1/4" FEP
TFE SLEEVE
IMPACTOR NOZZLE
TFE SPACER
IMPACTION DISK
"BLACK" COUPLERS
A
B
ANNULAR DENUDER
"RED" COUPLERS
BELL CONNECTOR
P
PRESSURE GUAGE
2-WAY VALVE(SS)
BYPASS LINE (NORPRENE TUBING)
FLOW CONTROLER
LIME-SODA SCRUBBER
47-mm FILTER
VACUUM

Figure 5. Impaction-surface exposure system.

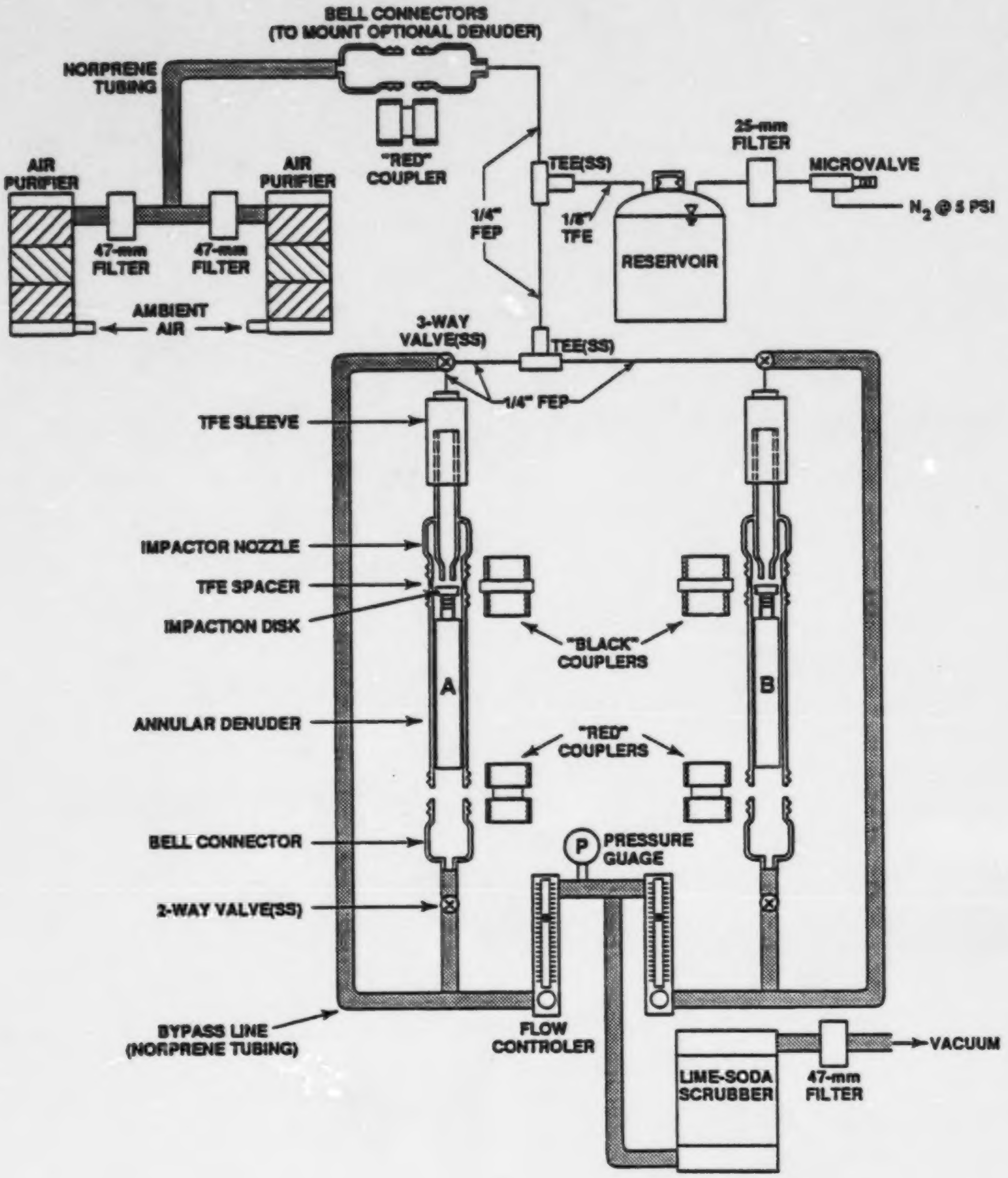
BELL CONNECTORS
(TO MOUNT OPTIONAL DENUDER)
NORPRENE
TUBING
"RED"
COUPLER
AIR
PURIFIER
AIR
PURIFIER
47-mm
FILTER
47-mm
FILTER
AMBIENT
AIR
TEE(SS)
1/4"
FEP
1/8"
TFE
25-mm
FILTER
MICROVALVE
N_2 @ 5 PSI
RESERVOIR
3-WAY
VALVE(SS)
TEE(SS)
1/4" FEP
TFE SLEEVE
IMPACTOR NOZZLE
TFE SPACER
IMPACTION DISK
"BLACK"
COUPLERS
A
B
ANNULAR DENUDER
"RED"
COUPLERS
BELL CONNECTOR
PRESSURE
GUAGE
P
2-WAY VALVE(SS)
BYPASS LINE
(NORPRENE TUBING)
FLOW
CONTROLER
LIME-SODA
SCRUBBER
47-mm
FILTER
VACUUM

Figure 6. Impacted-particle exposure system.

Before (Figure 5) or after (Figure 6) introduction of the reactive gas, the flow entered a stainless-steel Swagelock tee, which divided the flow into two streams feeding identical test sections (A and B). In each section, the flow first entered a stainless-steel 3-way valve, which permitted the flow to be sent through the test section or bypass it. The 3-way valve was connected to a TFE sleeve with 1/4" FEP tubing and stainless-steel Swagelock fittings. Each TFE sleeve was machined to accept a 1/4" NPT fitting on one end and to fit snugly over the inlet of an impactor nozzle wrapped with TFE pipe-thread tape.

The flow subsequently passed through the impactor nozzle, over the impaction disk, and through the denuder. Each denuder was coated to adsorb the gas of interest so that its actual concentration during each experiment could be determined. Black couplers (supplied by University Research Glassware) containing or holding a TFE-coated silicone spacer were used to connect the impactor nozzles to the denuders, and red couplers (GL30, Schott American, Yonkers, NY) were used to connect the denuders to the bell connectors.

Bypass lines were initially installed in earlier system designs incorporating diffusion tubes and diffusion vials of various types. These devices required a long time to reach equilibrium, which was upset each time the test section was disconnected to insert or remove a test specimen. As a result, massive slugs of the test gas would enter the test section each time the system was disturbed. The bypass lines greatly improved the situation but did not eliminate the problem entirely. Therefore, it was decided to abandon the use of diffusion tubes and diffusion vials holding concentrated solutions. A syringe pump was also tried, but the drops formed on the tip of the needle did not evaporate rapidly enough. Subsequently, the design shown in Figures 5 and 6 was adopted. This system was still subject to disruption by pressure changes (the pressure in the reservoir is influenced by the partial vacuum in the tee); but the disruptions were negligible due to the high flow rate of nitrogen through the reservoir and the relatively low concentration of reactive gas in the headspace of the reservoir. The bypass was left in place to minimize perturbation of the reservoir and to facilitate conditioning of the system prior to the start of an experiment.

A steady flow through each side of the system was separately maintained using flow controllers (Model 52-31-D-4-88, Scott Specialty Gases, Troy, MI) incorporating Brooks flow tubes (R-6-15-B). A pressure gauge permitted the exit pressure of the rotameters to be recorded so that the flowrates could be corrected for pressure. Before entering a vacuum pump, the flow was scrubbed to remove any acidic gases present (e.g., when using the bypass) and filtered to remove particles. The nominal (uncorrected) flowrate through each side of the system was 16.7 Lpm.

All tubing between the inlet bell connectors (used to mount the optional denuder on the inlet line) and the test sections was 1/4" FEP or TFE connected using stainless-steel Swagelock fittings. The tubing connecting the reservoir to the compressed nitrogen regulator and the stainless-steel tee was 1/8" TFE. The remaining tubing, used only where it was not in a position to produce artifacts, was Norprene synthetic rubber (3/8" ID x 5/8" OD).

In most of the experiments to examine chemical artifact formation by oil, grease, or filters, the test gas was introduced into only one side of the system (Figure 5), thereby leaving an unexposed system blank on the opposite side. When exposing particles to potentially reactive gases, an impaction disk loaded with particles was placed on one side of the system (Figure 6) and an identical disk not loaded with particles was placed on the other side to serve as an exposed blank (control sample). Another system, similar to that shown in Figure 6, was constructed to examine the volatilization of particles exposed to purified ambient air; this system differed from the others in that: 1) no side-stream flow was introduced; 2) no bypass lines were included; and 3) the air purifers were charged only with 4-8 mesh soda lime.

E. FIELD TESTS

Over the course of this study, a number of modifications to the sampling apparatus and the sampling protocol were made. Since short-term (1-4 hour) field sampling experiments using glass impactors, annular denuders, and filter packs were already being conducted as part of another study (EPA Grant No. R812280-01-0), these modifications were promptly tested and, if successful, incorporated into the operating procedure. Some of the resulting experiences are described herein (in Section 8: Results and Discussion); but the data for the short-term field tests will be included in the final report for the other study.

The goal of this study was to develop a procedure suitable for a 24-hr sampling period. Therefore, a 24-hr field test was conducted to determine the precision of the method. The procedure used is described in detail in Appendix A. Four identical sampling systems were mounted on the roof of a four-story building (Learned Hall) on the campus of Kansas University. The bent-tube inlets were turned in the direction of the prevailing wind (north to northwest) on the day of sampling; but the inlets were not moved as the winds shifted and the surrounding landscape produced a fair amount of turbulence, such that an isoaxial sampling condition could not be assumed. Mass flow controllers (Model FC-280, Tylan Corp., Torrance, CA), having an accuracy of ± 1% and a precision of ± 0.2%, were used to maintain a flow of 12.5 Lpm (STP: 25°C and 1 atm); prior to use they were cross-calibrated and found to agree within < 0.5%.

SECTION 8

RESULTS AND DISCUSSION

A. IMPACTOR CUT-POINT DETERMINATION

The modified 4.00-mm glass impactor was designed to have a theoretical aerodynamic cut-point diameter of 2.50 µm. Baxter et al. (1987) studied a similar 4.00-mm impactor, one having a glass impaction surface directly attached to the jet, and experimentally determined its cut point to be 2.64 µm. Other investigators (e.g., Marple et al., 1987) have also reported actual cut-points very close to the theoretical values for similarly designed impactors. However, the modifications made to the impaction surface in this study, especially the introduction of a 0.5-mm deep well on the top of the impaction disk (Figure 3), as well as the impactor's very high Reynolds number, raised questions concerning the actual performance of the impactor.

To determine whether the modified impactor would perform as predicted, its collection efficiency was examined in a series of wind-tunnel experiments involving uranine particles having aerodynamic diameters between 0.95 and 7.95 µm. In each of these experiments, the impactor (coupled to a bent-tube inlet) was mounted vertically in an upright position; a 13-mm polycarbonate filter was placed in the well and coated with 5 µL of silicone oil; and the flowrate was 12.5 Lpm (STP). The results are shown in Table 5 and Figures 7 and 8.

Table 5 shows the percentage of particle mass deposited on each sampling-system component for each particle size tested. Aerodynamic diameters (D_{AE}) were computed from physical diameters (D_p) assuming a particle density of 1.4 gm/L. The "inlet" fraction includes all particles deposited on the interior of the sharp-edged 90° bent-tube inlet, the interior of the inlet tube of the impactor nozzle, and the interior surface of the jet. The "nozzle wall" fraction includes only those particles collected on the exterior surface of the jet and the interior surface of the jet housing, which was coupled to the denuder. The other fractions are self explanatory. As expected, the fraction collected on the impaction disk increased with increasing particle size, while the fraction on the back-up filter decreased. However, in most cases there were measurable losses associated with the inlet, nozzle wall, spacer, and denuder.

In earlier experiments, it had been observed that particles collected on the impactor inlet were found primarily at the entrance to the jet, where the flow is constricted from 10-mm to 4.0 mm. To see whether such losses could be reduced, impactor nozzles having a more gently tapered transition from the inlet tube to the jet (10° vs 30°) were ordered and obtained from University

TABLE 5. FRACTIONAL COLLECTION BY SAMPLING SYSTEM COMPONENTS FOR VARIOUS PARTICLE SIZES

		Fractional Collection, %						Average Impaction-Surface Collection Efficiency, %	
D_p, µm	D_{AE}, µm	Inlet	Nozzle Wall	Impaction Disk	Spacer	Denuder	Back-up Filter	Overall*	Adjusted*
0.80	0.95	0.0	0.0	2.0	1.3	1.9	94.8	3.1±0.9	3.1±0.9
		0.8	0.0	3.8	3.7	4.4	87.3		
		1.5†	1.2	3.9	2.2	3.6	87.7		
		0.8	0.0	2.6	1.4	2.1	93.2		
1.70	2.01	0.3	0.4	29.2	14.4	6.5	49.2	34.6±7.7	34.8±7.7
		0.3†	0.5	43.4	14.9	7.8	33.1		
		0.6	0.4	31.3	10.5	4.8	52.4		
2.02	2.39	0.1	0.2	33.4	10.0	4.9	51.4	37.8±8.3	37.9±8.2
		0.1†	0.2	47.4	11.3	4.3	36.8		
		0.2	1.3	32.7	14.6	4.4	46.8		
2.36	2.79	0.0	0.3	52.9	16.8	5.5	24.5	60.6±7.1	60.7±7.2
		0.1†	0.3	66.9	11.9	5.6	15.2		
		0.7	0.3	61.9	10.3	6.6	20.2		
4.20	4.97	0.1	0.0	99.3	0.2	0.2	0.1	98.7±0.8	98.9±0.6
		0.0†	0.0	99.1	0.3	0.3	0.2		
		0.3	0.0	97.8	0.2	0.1	1.5		
6.72	7.95	0.5†	0.0	98.8	0.4	0.1	0.2	98.9±0.4	99.4±0.2
		0.1†	0.0	99.3	0.3	0.1	0.1		
		0.6†	0.0	98.6	0.3	0.2	0.3		

* The overall efficiency is the mass collected on the impaction disk divided by total mass entering the sampler; adjusted values were computed by subtracting the inlet losses from the total mass sampled.

† The nozzle used for this experiment was more gently tapered (at an angle of about 10°).

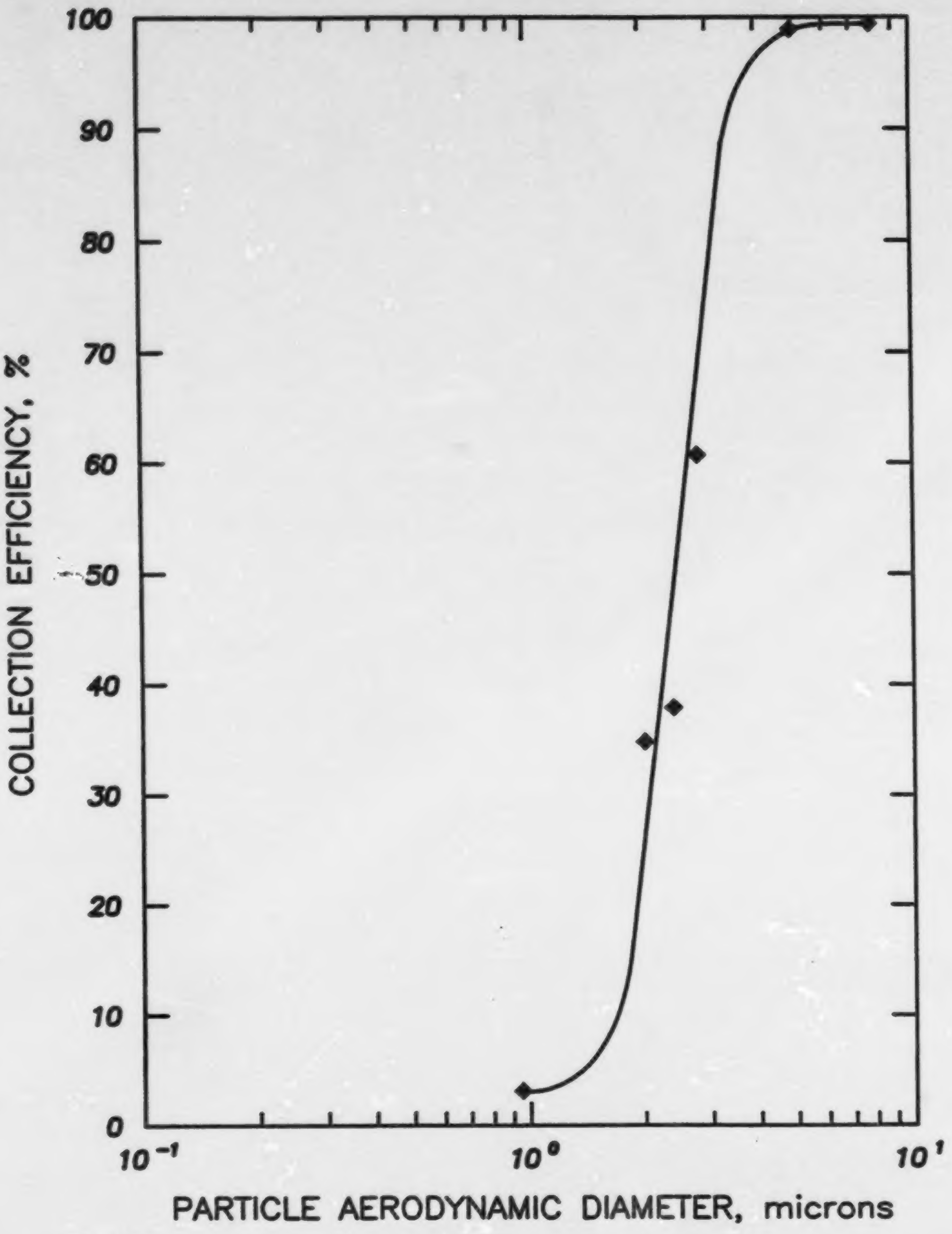

Figure 7. Adjusted collection efficiency of the modified impactor as a function of particle size.

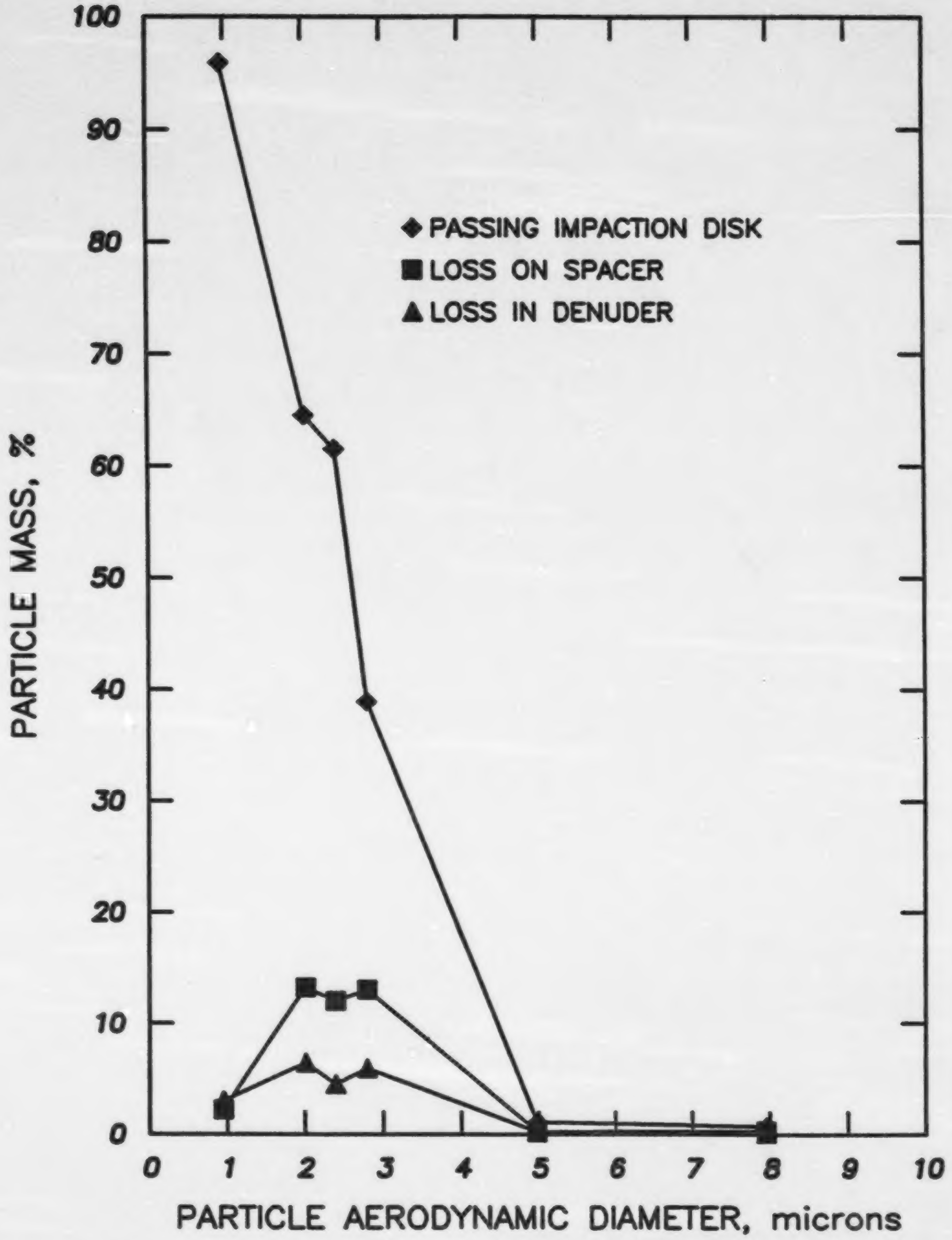

Figure 8. Particle losses on the spacer and in the denuder as a function of particle size.

Research Glassware. One of these nozzles was used for eight of the nineteen experiments described in Table 5. Since the data for the more gently tapered nozzle show no consistent trend relative to the other nozzles, it appears that the performance of the impactor is not significantly influenced by the taper of the inlet-to-jet transition. Therefore, the data for both nozzles were pooled in determining the cut point.

The average overall impaction-surface collection efficiency was calculated as the mass collected on the impaction disk divided by the entire mass entering the sampler. To determine the cut point of the impactor, the inpaction-surface collection efficiency values were adjusted by deducting the "inlet" losses from the total mass sampled, such that particles not having an opportunity to strike the impaction surface were excluded. Figure 7 shows the adjusted collection efficiency of the impactor as a function of particle size. The cut point (50% collection) was determined to be 2.51 μm (aerodynamic diameter) on the basis of a least-squares regression of average adjusted collection efficiency versus log (D_{AE}). A cut point of 2.52 μm was calculated using unadjusted collection efficiencies. Both values are nearly identical to the predicted value of 2.50 μm.

An examination of the data in Table 5 reveals that losses on the spacer and in the denuder tended to be substantially higher for particles having aerodynamic diameters close to the cut point. This relationship is clearly evident in Figure 8. It is not surprising that particles near the cut point size should be partially removed by impaction on the gasket or by deposition in the denuder, the latter probably due to turbulent eddies in the inlet section of the denuder. These results suggest that the concentrations of gaseous species determined using the denuders will be biased high, due to collection of a small fraction of coarse particles; but this bias should be insignificant unless the species of interest are heavily concentrated in a size fraction close to the 2.5-μm cut point.

The data in Table 5 also demonstrate that very little particle bounce occurred when large particles were collected on oiled polycarbonate membranes. Bounce was less than about 1% for 4.97 and 7.95 μm particles, even if it is assumed that all of the particles passing the impaction disk actually impacted on the disk. Particle bounce was also examined as a function of the type of impaction surface and as a function of mass loading, as discussed in Section 8D.

Also noteworthy are the inlet losses reported in Table 5. With only a single exception, particle loss in the inlet (including both the bent-tube inlet and the impactor nozzle inlet) was less than 1%. Particle loss averaged 0.4% for 7.95-μm particles sampled isoaxially through a bent-tube inlet. This is in marked contrast to the results obtained during non-isoaxial sampling, as discussed in the following paragraphs.

B. NON-ISOAXIAL SAMPLING

Two non-isoaxial sampling tests were conducted using ammonium-sulfate particles with aerodynamic diameters of 8.0 μm. In each test, two 4.0-mm straight-inlet impactor nozzles (without impaction disks) were coupled directly to back-up filters, placed in the wind tunnel, and oriented at various angles (in the vertical plane) from the on-coming wind direction. Also placed in the wind tunnel during each test were two sampling filters connected to sharp-edged bronze nozzles operated under isoaxial and isokinetic flow conditions to accurately determine the average particle concentration in the wind tunnel test section. The sampling angles of the impactors during the first test were 0° (isoaxial) and 45°. The sampling angles of the impactors during the second test were 80° and 90°. The actual flowrate was 11.7 Lpm (STP).

The fractional collection results for these tests are presented in Table 6. The data show that as the sampling angle increased away from isoaxial there was a corresponding decrease in sampling efficiency for 8.0-μm particles, as expected based on the work of previous investigators (e.g., Wiener *et al.*, 1984). The drastic decrease in collection efficiency for the orthogonal (90°) position indicates that elutriation is predominating at the 8.0-μm particle size. This is supported by the results from several flow visualization tests that were conducted using a simple smoke-wire to generate flow streamlines. The two flow visualization tests depicted in Figure 9 clearly show the small regional sampling influence that is available under orthogonal sampling conditions.

Inlet losses increased substantially under non-isoaxial sampling conditions (Table 6), in one case (80°) exceeding 50% of the mass sampled. The 3% loss under isoaxial sampling conditions was much greater than that observed using sharp-edged inlets, even though the sharp-edged inlets were bent (Figure 1 and Table 5). The higher loss could be due to a difference in particle composition or other factors, but is most likely due to the use of a blunt-tipped inlet.

TABLE 6. FRACTIONAL COLLECTION RESULTS FOR NON-ISOAXIAL SAMPLING TESTS WITH 8.0-μm AERODYNAMIC-DIAMETER AMMONIUM-SULFATE PARTICLES

	Fractional Amount Collected, %		
Sampling Angle*	Impactor Inlet	Back-up Filter	Collection Relative To Total Possible†
0°	3.0	97.0	99.1
45°	7.5	92.5	90.5
80°	73.6	26.4	28.7
90°	45.0	55.0	8.5

* 0° = Isoaxial
† Based on total mass collected on isoaxial, isokinetic filters.

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Figure 9. Flow streamlines for a 4.00-mm glass impactor at a nominal flowrate of 16.7 Lpm with a wind speed of 800 fpm.

Important implications of these results include the following:

1) Since large particles can be elutriated under non-isoaxial sampling conditions, accurate sampling of large particles will require isoaxial or near-isoaxial sampling;

2) Since large particles are effectively elutriated under orthogonal sampling conditions, orienting a straight impactor inlet in a vertical inverted position is an effective way to avoid entrainment of large particles and to limit the mass loading on the impaction disk in situations where the impactor is used only to remove the coarse fraction rather than to sample it; and

3) The increased inlet losses observed under non-isoaxial sampling conditions represent a potentially significant source of chemical artifacts in that the particles collected on the inlet may volatilize or may interact chemically with reactive gases flowing through the inlet.

C. INLET LOSSES, PARTICLE BOUNCE, AND IMPACTOR ORIENTATION

Description of the Problems Faced

Inlet losses pose several significant problems in regard to the quantitative measurement of large nitrogen- and sulfur-bearing aerosols. The most obvious problem is that large particles collected on the inlet are not included in the large-particle fraction collected on the impaction disk. Thus, they must be removed from the inlet and analyzed separately (or combined with the impacted fraction), thereby complicating the procedure. A second problem is that gaseous constituents may also adsorb on the inlet; and while the amounts adsorbed may not represent a significant fraction of the gaseous species sampled by the denuder, they may be very significant in comparison to the amounts associated with large particles inadvertantly trapped on the inlet. It is not clear whether constituents washed form the inlet should be included with the large-particle fraction or attributed to artifact formation. A third problem is that large particles collected in the inlet are not removed from the gas stream and can potentially react with various gases to form chemical artifacts.

Because of the potential importance of inlet losses, they were examined in a number of experiments and a substantial effort was made to minimize them. The non-isoaxial sampling experiments (see Section 8B) were among the first in which inlet losses were examined. Based on these results, it was decided to develop a sampling protocol based on isoaxial sampling conditions. Such conditions can be achieved by mounting the impactor horizontally and facing it into the wind (perhaps oriented by a wind vane) or by mounting the impactor vertically and attaching to it a device capable of collecting a sample isoaxially and then transmitting it without loss into the impactor nozzle.

Horizontally Mounted Impactors

The possibility of using a horizontally mounted impactor was examined first, with primary consideration given to two potential problems: large-particle sedimentation and particle bounce. Sedimentation of the fine-particle fraction in the denuder was dismissed as a potential problem because: 1) calculations based on fundamental principles predicted losses of much less than 1% (i.e., negligible losses in view of the fact that the concentrations of the gaseous species of interest usually exceed those of the fine particle fraction); and 2) even if such losses were found to occur, it would not be difficult to combine a horizontal impactor with a vertically mounted denuder tube. Large particles, however, could potentially settle out in a horizontal inlet; and high-mass loadings of large particles could result in particle bounce using greased or lightly oiled surfaces. Excess oil can prevent particle bounce at high mass loadings, but it is difficult to maintain excess oil on a vertical impaction surface.

To determine whether 8-μm particles would be deposited in a horizontally mounted glass-impactor inlet and to simultaneously examine the bounce and particle-loading characteristics of the system using silicone grease, tests were conducted using a horizontally mounted sampling system employing a modified 4.0-mm glass impactor, a silicone-grease-saturated membrane filter, an annular denuder, and a backup filter. The horizontal position of the impactor-denuder system facilitated employment of isoaxial and isokinetic sampling conditions. Uranine particles with an aerodynamic diameter of 8.34 μm were generated for these tests. Run times for the tests ranged from 20 to 360 minutes so that particle loadings on the impaction surface could be increased. Table 7 presents the fractional collection results of these tests.

Loss of particles within the horizontally mounted sampling system was evident in the impactor inlet, on the spacer between the impactor and the denuder tube, and in the denuder tube (see Table 7). A significant drop in the fractional collection efficiency of the grease-coated impaction surface occurred for run times exceeding 120 minutes, indicating that the particle loading limit for the particle size tested had been reached. The impacted particles were observed to cover a circular area approximately 3.7 mm in diameter, similar to what has been observed for field samples collected as part of another study. It takes only about 55 μg of 8.34 μm particles to cover an area of this size with a monolayer of particles, so it is not surprising that significant bounce occurred at loadings of 31 and 48 μg.

The losses in the horizontally mounted inlets were significant, but may have been due to the use of unsharpened inlets rather than to sedimentation. In any event, since winds at the earth surface travel primarily in a horizontal direction, the inlet losses associated with isoaxial sampling will be the same regardless of whether the rest of the sampling system is oriented vertically or horizontally. Such losses can be minimized by using short, sharp-edged sampling tubes and isokinetic sampling rates (e.g., Fissan and Schwientek, 1987; Pui _et al._, 1987; Lipatov _et al._, 1988).

Since particle bounce is a function of particle size and composition (e.g., Hinds _et al._, 1985; Wang and John, 1987), particles differing in size

TABLE 7. FRACTIONAL COLLECTION EFFICIENCIES OF HORIZONTALLY MOUNTED SAMPLING-SYSTEM COMPONENTS UNDER INCREASING PARTICLE LOADING CONDITIONS*

Run Time (min.)	Fractional Collection, % Inlet	Nozzle Wall	Impaction Disk	Denuder	Back-up Filter	Total Mass (μg)	Impacted Mass (μg)	Adj. Imp. Coll. Eff. (%)
20	8.8	0.4	90.0	0.3	0.5	2.29	2.06	98.7
20	7.4	0.2	91.9	0.2	0.3	3.05	2.80	99.2
33	8.1	0.2	91.6	0.0	0.1	4.42	4.05	99.7
120	1.8	0.7	93.2	1.2	3.1	13.60	12.67	94.9
270	1.9	3.1	82.0	4.4	8.6	37.60	30.84	83.6
360	2.0	1.7	84.9	3.2	8.2	56.96	48.38	86.6

* Isoaxial sampling of uranine particles having an aerodynamic diameter of 8.34 μm; silicone-grease-coated impaction disk.

and composition from 8.34-μm uranine particles can be expected to produce results quantitatively different from those in Table 7. Moist or oily particles would not be expected to bounce as much as uranine particles, but dry crystalline particles might bounce to a much greater extent. However, particles of a variety of types and sizes will be encountered in the field, so a sampler designed for field use must be capable of sampling particles that tend to bounce.

An examination of the data in Table 7 reveals that particle bounce using a silicone-grease-coated impaction disk was about 1% for particle mass loadings less than 5μg. This data, as well as a wealth of information previously published by other investigators, suggests that grease can eliminate particle bounce at low mass loadings. However, high mass loadings are expected to occur from time to time in the field. For example, if air having a total particle concentration of only 20 $\mu g/m^3$ is sampled at a rate of 16.7 Lpm for 24 hours, and if only 10% of the particles are coarse (>2.5 μm), the mass loading on the impaction disk will be 48 μg, more than enough to create conditions suitable for particle bounce. Hence, a sampler designed for field use must be capable of handling or avoiding high mass loadings.

Potential solutions to the particle bounce problem at high mass loadings include: 1) using shorter sampling times; 2) using a rotating impaction surface, such that the particles are spread over a larger area (the void space in the inner tube of the denuder offers a suitable location for mounting a small motor); and 3) using oil instead of grease, since oil can potentially wick up onto and coat the surfaces of previously deposited particles.

The possibility of using oil-saturated porous glass impactions disks in a horizontally mounted sampling system was explored, but several problems were encountered. The first problem noted was that oil leaked out through the holes in the TFE disk when a removable porous glass disk was used. This was undesirable for three reasons: 1) it was messy; 2) it eliminated the possibility of gravimetric analysis of the impacted particle mass; and 3) it left the top surface of the disk unsaturated. Therefore, it was decided to use impaction disks having a coarse non-removable porous glass disk (see Section 5A) in an experiment involving three horizontally mounted sampling systems operating simultaneously under isokinetic and isoaxial conditions. The results of this experiment were very inconsistent (i.e., there was a large variation in the mass collected on the impaction surface); and it was subsequently determined that the probable cause of the poor results was that oil flowed (sideways) off the impaction surface under the force of gravity.

These problems were discussed with one investigator who recommended wiping off the excess oil, but it was feared that this might contaminate the disk. Consideration was given to reducing the amount of oil used on the impaction disk, but it was feared that using less oil might decrease the particle collection efficiency (i.e., increase particle bounce); and subsequent experiments (discussed below) confirmed that this was indeed the case. Since it did not appear that the problems associated with a horizontally mounted sampling system could be readily resolved, attention was shifted to the vertically mounted system.

Vertically Mounted Impactors

The major problem to be overcome using a vertically mounted impactor is the loss of particles as the flowstream is changed from isoaxial (horizontal) to vertical prior to entering the impactor. A variety of inlet configurations, including circular bent-tube inlets, rectangular (slotted) bent-tube inlets, and various proprietary designs, were considered vis-a-vis their potential to avoid such losses. It was decided to proceed using circular bent-tube inlets due to their simplicity, low cost, and availability, and to the lack of any clear advantage of using more sophisticated inlets.

Particle deposition in a bent-tube inlet at a fixed sampling rate is primarily governed by the density and diameter of the particles, so it is clear that substantial losses will occur for particles above a certain size. Such losses can be theoretically predicted (Pui et al., 1987); and it was predicted that a bent-tube inlet having the same internal diameter (1 cm) as the impactor inlet would cause minimal loss of 8-µm particles. It was decided to experimentally verify this before attempting to sample larger particles.

The first 90°-bent-tube inlets tested were blunt-tipped PTFE/FEP-coated glass inlets (supplied by University Research Glassware). The horizontal leg and bend of each inlet had an ID of 1.1 cm, while the lower portion of the vertical leg was enlarged to slip over the inlet of the impactor nozzle. The bottom of the vertical leg was threaded to permit the bent tube to be tightly affixed to the impactor nozzle by means of a compression fitting (Sovirel 22).

Two tests were conducted to measure particle loss in the blunt bent-tube inlets and to simultaneously examine the collection efficiency of the impactor under high mass loading conditions when using oil. Two blunt bent-tube inlets were attached to vertically mounted sampling systems each comprised of an impactor, denuder tube, and back-up filter. The impaction disks (fitted with coarse-pored fritted glass disks) were saturated with silicone oil, and the sampling systems were mounted side-by-side in the wind tunnel. Uranine particles with an aerodynamic diameter of 8.34 μm were generated; and the run time for the second test (720 minutes) was double that of the first (360 minutes) so that the particle loads of the two tests would be significantly different. Table 8 presents the fractional collection results for these tests.

TABLE 8. FRACTIONAL COLLECTION RESULTS FOR VERTICALLY MOUNTED SAMPLING-SYSTEM COMPONENTS USING BLUNT BENT-TUBE INLETS AND SILICONE OIL*

	Fractional Collection Amount, %								
Test No.	Bent Tube	Imp. Nozzle	Imp. Disk	Spacer	Denuder	Back-up Filter	Total Mass (μg)	Impacted Mass (μg)	Adj. Imp. Coll. Eff. (%)
1A	6.9	0.3	91.4	0.1	0.4	0.9	59.19	54.08	98.5
1B	11.2	0.1	87.0	0.4	0.2	1.0	61.28	53.30	98.2
2A	6.5	0.6	92.4	0.1	0.1	0.3	85.59	79.09	99.5
2B	11.0	1.9	86.0	0.2	0.3	0.6	91.33	78.59	98.7

* Uranine particles having an aerodynamic diameter of 8.34 μm were impacted on silicone-oil-saturated coarse-pored fritted glass disks at a sampling flowrate of 11.7 Lpm (STP).

The data show that there was a significant amount of particle deposition in the bend. Pui et al. (1987) have suggested that particle deposition efficiency in bends should approach zero for the finite Stokes numbers of 0.2 at Re = 1000 and 0.4 at Re = 100. The flow Reynolds number (Re) of the inlet bend used in these tests was 1490 (based on the actual flowrate) and the particle Stokes number was 0.121. Therefore, particle deposition under these conditions should have been minimal. The deposition which did occur, however, can be attributed to: 1) the presence of an abrupt transition from the bend into the straight inlet section of the impactor (particles were visible on the lip of the impactor inlet, which extended to within one inch of the bend); and 2) the bluntness of the bent-tube inlet, which undoubtedly increased turbulence in the bent tube.

To reduce deposition in the bent-tube inlet, it was redesigned as shown in Figure 1. The newer design featured a sharp-edged opening and a tube of the same inside and outside diameter as the glass-impactor inlet, such that the two could be butted together and held in place using a cold-press TFE sleeve. Losses of less than one percent were experienced using this inlet, as noted earlier (Table 5 and Section 8A).

A comparison of the results in Tables 7 and 8 reveals that there were significant differences between oil and grease in regard to the impactor collection efficiencies (adjusted for inlet losses) obtained under high (> 30 µg) mass loadings. Less than 2% bounce occurred using silicone oil, versus 13-16% using silicone grease. Even less bounce occurred when using an oiled membrane filter rather than an oiled porous glass disk (Table 5 versus Table 8).

As shown in Table 8, significantly higher losses occurred in inlet B during both tests. This suggests that there are system specific performance characteristics that must be considered if these particular inlets are to be used. Such inconsistency was not observed using the newer bent-tube inlet design (Figure 1 and Table 8A), and losses were minimal for particle sizes less than 10 µm (aerodynamic diameter).

Several experiments examined bent-tube inlet losses for particles larger than 10 µm. The first such experiment employed bent tubes fashioned from thin-walled glass tubing (1 cm ID) with fire-polished ends. As shown in Table 9, particle losses in the bent tubes for 15.2-µm ammonium sulfate particles were very substantial, averaging 50% of the mass sampled. In another experiment involving 26.5-µm uranine particles and the sharpened bent-tube inlets depicted in Figure 1, inlet losses averaged 93% (Table 10). Large particles can be rinsed from the inlets and analyzed, but there is a significant potential for artifact formation as a result of gas/particle interactions. Hence, better sampling methods are clearly needed for particles larger than 10 µm.

Sampling of particles larger than 10 µm might be accomplished in several ways. One way would be to use the inlet bend itself as an impactor, perhaps with a removable oil or grease-coated section to permit recovery of the particles. One such design was attempted; an inlet having two straight cylindrical holes at right angles to each other and a removable plug in the bend was machined from pure TFE. The plug was coated with silicone grease prior to each use. Unfortunately, in 14 of 15 tests involving uranine particles ranging in size from 0.62 to 30.9 µm (aerodynamic diameter), less than one half of the particles collected by the inlet were found on the removable plug. The major problem was thought to be the poor aerodynamic design of the inlet; and particle bounce may also have been a significant factor. Other designs, including a 90° bent square or rectangular inlet with an elongated plug were considered; but after discussions with the project officer, efforts along these lines were discontinued so that more attention could be given to other aspects of the research.

It is worth noting that substantial particle bounce was observed using oiled porous glass disks (Table 9), whether or not the disks were covered with a membrane filter. In contrast, much less particle bounce was observed using oiled membrane filters (Table 10). Additional experiments were conducted to

TABLE 9. FRACTIONAL COLLECTION OF 15.2-μm AMMONIUM-SULFATE PARTICLES SAMPLED USING THIN-WALLED GLASS BENT-TUBE INLETS*

	Run No. 1		Run No. 2		Run No. 3	
	μg	%	μg	%	μg	%
Bent-Tube Inlet	2.69	48.4	2.28	52.1	2.67	50.0
Impactor Inlet	0.00	0.0	0.00	0.0	0.21	3.9
Nozzle Wall	0.14	2.5	0.08	1.8	0.14	2.6
Impaction Disk	2.60	46.8	1.83	41.8	2.28	42.7
Spacer	0.00	0.0	0.00	0.0	0.00	0.0
Denuder	0.00	0.0	0.00	0.0	0.00	0.0
Back-up Filter	0.13	2.3	0.19	4.3	0.04	0.7
Total Mass	5.56	100.0	4.38	100.0	5.34	99.9
Adjusted Impactor Collection Efficiency†		90.7		87.3		85.6

* Sampling flowrate = 11.7 Lpm (STP); 90° bent-tube inlets (constructed from thin-walled glass and having fire-polished ends) inserted into wind tunnel; porous glass disks coated with 100 μL silicone oil and, in runs 2 and 3, overlain with a membrane filter; sampling system mounted vertically; D_{AE} = 15.2 μm.

† With inlet losses deducted from total mass.

TABLE 10. FRACTIONAL COLLECTION OF 26.5-μm URANINE PARTICLES SAMPLED USING SHARP-EDGED 90° BENT-TUBE INLETS*

	Run No. 1		Run No. 2		Run No. 3	
	μg	%	μg	%	μg	%
Inlet	13.556	92.5	17.103	95.7	15.444	90.8
Nozzle Wall	0.000	0.0	0.021	0.1	0.018	0.1
Impaction Disk	1.093	7.5	0.746	4.2	1.539	9.0
Spacer	0.000	0.0	0.006	<0.1	0.000	0.0
Denuder	0.007	<0.1	0.000	0.0	0.008	<0.1
Back-up Filter	0.000	0.0	0.000	0.0	0.000	0.0
Total Mass	13.56	>100.0	17.10	>100.0	15.44	>99.9
Adjusted Impactor Collection Efficiency†		99.4		96.5		98.3

* Sampling flowrate = 11.7 Lpm (STP); particles impacted onto membrane filters oiled with 80, 30, and 10 μL of silicone oil, respectively; sampling system mounted vertically; D_{AE} = 26.5 μm.

† With inlet losses deducted from total mass.

examine particle bounce on oiled surfaces in more detail, as described in the following section.

D. PARTICLE BOUNCE AND MASS LOADING ON OILED SURFACES

Experiments were conducted to examine the particle bounce properties of oiled polycarbonate filters and porous glass impaction disks. Earlier results (including those discussed in subsection C) had conclusively shown that a very significant amount of bounce occurred when particles were impacted on grease applied to a polycarbonate filter, a solid glass impaction disk, or a TFE impaction disk. However, an average adjusted impactor collection efficiency of 98.7% had been observed using porous glass disks saturated with silicone oil (Table 8), and even better results had been obtained using oiled polycarbonate filters (Table 5). Therefore, it was decided to focus primarily on oil. Silicone oil was used for all but one of these experiments, and was selected for the reasons discussed in subsequent subsections of this report.

In preliminary tests involving the use of silicone oil, it was determined that the oil could easily be blown off a TFE impaction disk, even one having a recessed area (well) on top; and that a support medium (e.g., a membrane filter or a sintered metal or porous glass disk) would have to be used to prevent loss of oil. It was also observed that the force of the jet would push the oil away from the impaction area, leaving a "dry" spot, and force it toward the edge of the recessed area on top of the impaction disk. Interestingly, the surface tension of the oil was high enough that oil pushed above the level of the rim on top of the impaction disk was not lost as long as the jet velocity was increased gradually. Up to 80 µL of silicone oil placed on top of a polycarbonate filter could be retained in a 77-µL well at a sampling rate of 12.5 Lpm.

The experiments described in this subsection of the report were intended to address the following questions:

1) Does oil placed on a polycarbonate membrane filter give as good a collection efficiency as an oil saturated porous glass disk, or does the "dry" area promote particle bounce?

2) How much oil is needed, using either a polycarbonate filter or a porous glass disk, to prevent particle bounce?

3) Does it make a difference whether oiled porous glass disks are used in an inverted or upright position?

4) Are salt particles collected as effectively as uranine particles?

5) Does particle bounce increase with mass loading when using oil?

6) Is particle bounce influenced by the particle loading rate, i.e., the particles in the air sampled?

7) Where in the system are the particles that bounce collected?

The results of experiments conducted to address these questions are presented in Tables 11 through 18 and Figures 10 and 11.

Oiled Polycarbonate Membrane Filters

The data in Table 11 demonstrate that an 80 µL pool of silicone oil underlain by a polycarbonate filter can effectively collect 8.34-µm uranine particles at a mass loading approaching a monolayer. The inlet loses were a bit high (as a result of using blunt-tipped bent-tube inlets), but virtually no particle bounce occurred. The average adjusted impactor collection efficiency was 99.9%, surpassing the earlier performance of the oil saturated porous glass disks (Table 8). Interestingly, in all three runs, no particle mass was found on the interior wall of the nozzle, suggesting that particles collected on the nozzle wall in other experiments may have bounced off the impaction surface before being deposited on the nozzle wall. It was for this reason that only the inlet losses (i.e., those resulting from collection of particles in the impactor inlet and jet) and not nozzle-wall losses were deducted from the total mass in computing adjusted impactor collection efficiencies.

During the experiments summarized in Table 11, oil was observed on the rim of the impaction disk, and it appeared that there was significant potential for oil loss into the denuder. Therefore, use of smaller amounts of oil was considered. It was determined that a 13-mm polycarbonate filter could be saturated with as little as 2 µL of silicone oil, but it was difficult to apply such a small quantity and there appeared to be no reason to use less than 5 µL of oil. Using 5 µL of oil, a thin film of oil remained visible on top of the filter but the potential for spilling the oil was minimal.

The collection of 7.9-µm uranine particles impacted on a polycarbonate filter coated with 5 µL of silicone oil was examined as a function of mass loading. By using a pipe rather than the wind tunnel, it was possible to obtain very high mass loadings in a short period of time. As shown in Table 12, high collection efficiencies were obtained, even at mass loadings approaching 3 mg, representing about 50 layers of particles on the 3.7-mm area actually impacted by particles. Hence, the oil effectively wicked over the "dry" spot on the filter and onto the impacted particles. There appeared to be a trend toward slightly lower collection efficiencies at the highest mass loadings, but it should be noted that the particle concentration exceeded 5,000 µg/m^3 for the 40-minute exposure; and at this loading rate particles may have been impacting on top of previously impacted particles before the oil could wick up and coat them. In any event, the collection efficiency was clearly excellent.

Particle bounce is known to be strongly influenced by the physical/chemical properties of the particles being collected (e.g., Hinds et al., 1985; Wang and John, 1987). Since uranine particles are light and organic, their bounce properties might be very different from those of inorganic salts. Indeed, such differences were clearly evident during preparation of various types of particles to examine their reactivity (Section

TABLE 11. FRACTIONAL COLLECTION OF 8.34-µm URANINE PARTICLES IMPACTED ON AN IMPACTION DISK HOLDING 80 µL OF SILICONE OIL*

	Run No. 1		Run No. 2		Run No. 3	
	µg	%	µg	%	µg	%
Inlet	3.59	8.2	5.61	14.0	2.78	6.9
Nozzle Wall	0.00	0.0	0.00	0.0	0.00	0.0
Impaction Disk	40.01	91.7	34.35	85.9	37.22	93.0
Spacer	0.01	<0.1	0.01	<0.1	0.01	<0.1
Denuder	0.01	<0.1	0.01	<0.1	0.01	<0.1
Back-up Filter	0.02	<0.1	0.01	<0.1	0.00	0.0
Total Mass	43.64	>99.9	39.99	>99.9	40.02	>99.9
Adjusted Impactor Collection Efficiency†		99.9		99.9		99.9

* Sampling flowrate = 11.7 Lpm (STP); 90° blunt-tipped bent-tube inlet inserted into wind tunnel; system mounted vertically; D_{AE} = 8.34 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 12. FRACTIONAL COLLECTION AS A FUNCTION OF MASS LOADING FOR 7.9-µm URANINE PARTICLES IMPACTED ON A MEMBRANE FILTER COATED WITH 5 µL OF SILICONE OIL*

Exposure Time:	5 Minutes		10 Minutes		20 Minutes		40 Minutes	
Mass Collected:	µg	%	µg	%	µg	%	µg	%
Inlet	0.66	0.5	0.24	0.1	7.45	0.6	114.74	3.9
Nozzle Wall	0.03	<0.1	0.06	<0.1	0.38	<0.1	3.32	0.1
Impaction Disk	124.30	98.8	233.82	99.3	1285.96	98.6	2772.46	94.9
Spacer	0.49	0.4	0.80	0.3	4.50	0.3	10.95	0.4
Denuder	0.12	0.1	0.21	0.1	2.31	0.2	3.93	0.1
Back-up Filter	0.20	0.2	0.22	0.1	3.41	0.3	15.82	0.5
Total Mass	125.80	>99.9	235.35	>99.9	1304.01	100.0	2921.22	99.9
Adjusted Impactor Collection Efficiency†		99.4		99.5		99.2		98.9

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind pipe; sampling system mounted vertically; D_{AE} = 7.9 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 13. FRACTIONAL COLLECTION AS A FUNCTION OF MASS LOADING FOR 7.7-µm SODIUM-CHLORIDE PARTICLES IMPACTED ON A MEMBRANE FILTER COATED WITH 5 µL OF SILICONE OIL*

Exposure Time:	5 Minutes		10 Minutes		20 Minutes		40 Minutes	
Mass Collected:	µg	%	µg	%	µg	%	µg	%
Inlet	0.00	<0.1	0.82	0.1	25.53	1.4	119.40	4.0
Nozzle Wall	0.74	0.3	0.40	0.1	0.43	<0.1	6.89	0.2
Impaction Disk	213.67	98.5	739.37	98.9	1839.68	98.1	2861.72	94.8
Spacer	1.66	0.8	5.42	0.7	5.69	0.3	5.32	0.2
Denuder	0.58	0.3	0.91	0.1	1.57	0.1	14.19	0.5
Back-up Filter	0.30	0.1	0.89	0.1	2.34	0.1	12.48	0.4
Total Mass	216.95	100.0	747.81	100.0	1875.24	100.0	3020.00	100.1
Adjusted Impactor Collection Efficiency†		98.5		99.0		99.5		98.6

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind pipe; sampling system mounted vertically; D_{AE} = 7.7 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 14. FRACTIONAL COLLECTION AS A FUNCTION OF MASS LOADING FOR 7.9-µm URANINE PARTICLES IMPACTED ON A POROUS GLASS DISK COATED WITH 20 µL OF SILICONE OIL*

Position:	Upright				Inverted			
Exposure Time:	10 Minutes		20 Minutes		10 Minutes		20 Minutes	
Mass Collected:	µg	%	µg	%	µg	%	µg	%
Inlet	0.06	<0.1	5.77	0.6	42.63	9.5	75.25	4.6
Nozzle Wall	3.35	2.4	16.10	1.7	7.83	1.7	21.32	1.3
Impaction Disk	33.16	23.9	355.35	37.2	153.60	34.1	827.48	51.1
Spacer	6.62	4.8	76.27	8.0	41.55	9.2	90.95	5.6
Denuder	74.76	53.8	256.72	26.8	60.45	13.4	241.44	14.9
Back-up Filter	20.89	15.0	246.09	25.7	144.90	32.1	363.96	22.5
Total Mass	138.84	99.9	956.30	100.0	450.96	100.0	1620.40	100.0
Adjusted Impactor Collection Efficiency†		23.9		37.4		37.7		53.6

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind pipe; sampling system mounted vertically; coarse-pored fritted glass disk coated with oil by adding 200 µL of a 10% solution of silicone oil in pentane; D_{AE} = 7.7 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 15. FRACTIONAL COLLECTION OF 7.9-µm URANINE PARTICLES IMPACTED AT MODERATE MASS LOADING ON A POROUS GLASS DISK COATED WITH 20 µL OF SILICONE OIL*

Position:	Upright				Inverted			
Exposure Time:	30 Seconds		60 Seconds		30 Seconds		60 Seconds	
Mass Collected:	µg	%	µg	%	µg	%	µg	%
Inlet	0.21	0.8	0.27	0.5	1.49	4.6	2.39	3.7
Nozzle Wall	0.50	1.8	1.25	2.4	1.07	3.3	1.53	2.4
Impaction Disk	11.35	41.9	16.88	31.8	14.02	43.0	29.89	46.3
Spacer	0.97	3.6	1.93	3.6	2.72	8.3	3.57	5.5
Denuder	9.44	34.8	20.79	39.2	7.72	23.7	10.34	16.0
Back-up Filter	4.62	17.1	11.93	22.5	5.58	17.1	16.81	26.0
Total Mass	27.09	100.0	53.05	100.0	32.60	100.0	64.53	99.9
Adjusted Impactor Collection Efficiency†		42.2		32.0		45.1		48.1

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind pipe; sampling system mounted vertically; porous glass disk coated using 200 µL of a 10% solution of silicone oil in pentane; D_{AE} = 7.7 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 16. FRACTIONAL COLLECTION OF 7.9-µm URANINE PARTICLES IMPACTED AT LOW MASS LOADING ON A POROUS GLASS DISK COATED WITH 20 µL OF SILICONE OIL*

Exposure Time:	20 Minutes		40 Minutes	
Mass Collected:	µg	%	µg	%
Inlet	0.167	3.6	0.375	4.0
Nozzle Wall	0.093	2.0	0.211	2.3
Impaction Disk	2.390	51.2	4.558	48.9
Spacer	0.139	3.0	0.351	3.8
Denuder	1.466	31.4	1.973	21.2
Back-up Filter	0.417	8.9	1.845	19.8
Total Mass	4.672	100.1	9.313	100.0
Adjusted Impactor Collection Efficiency†		53.1		50.9

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind tunnel; system mounted vertically in an inverted position; disk coated using 200 µL of 10% silicone oil in pentane; D_{AE} = 7.9 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 17. FRACTIONAL COLLECTION OF 7.9-µm URANINE PARTICLES IMPACTED AT LOW MASS LOADING ON A POROUS GLASS DISK COATED WITH 50 µL OF SILICONE OIL*

Exposure Time:	20 Minutes		20 Minutes	
Mass Collected:	µg	%	µg	%
Inlet	0.230	4.6	0.338	8.1
Nozzle Wall	0.063	1.3	0.063	1.5
Impaction Disk	3.416	67.9	2.794	66.6
Spacer	0.076	1.5	0.081	1.9
Denuder	0.941	18.7	0.570	13.6
Back-up Filter	0.306	6.1	0.348	8.3
Total Mass	5.032	100.1	4.194	100.0
Adjusted Impactor Collection Efficiency†		71.1		72.5

* Sampling flowrate = 12.5 Lpm (STP); straight (elutriator) inlet inserted orthogonally into wind tunnel; sampling system mounted vertically in an inverted position; disk coated using 500 µL of a 10% solution of silicone oil in pentane; D_{AE} = 7.9 µm.

† Inlet losses were deducted from the mass sampled.

TABLE 18. FRACTIONAL COLLECTION AS A FUNCTION OF MASS LOADING FOR 7.9-µm URANINE PARTICLES IMPACTED ON A POROUS GLASS IMPACTION DISK SATURATED WITH MINERAL OIL*

Exposure Time:	30 Seconds		20 Minutes	
Mass Collected:	µg	%	µg	%
Inlet	0.20	1.7	43.12	5.3
Nozzle Wall	0.02	0.2	0.65	0.1
Impaction Disk	11.54	95.9	756.48	92.6
Spacer	0.03	0.2	2.24	0.3
Denuder	0.18	1.5	7.46	0.9
Back-up Filter	0.06	0.5	6.96	0.9
Total Mass	12.03	100.0	816.91	100.1
Adjusted Impactor Collection Efficiency†		97.6		97.7

* Sampling flowrate = 12.5 Lpm (STP); sharp-edged 90° bent-tube inlet inserted into wind tunnel; sampling system mounted vertically; D_{AE} = 7.9 µm.

† Inlet losses were deducted from the mass sampled.

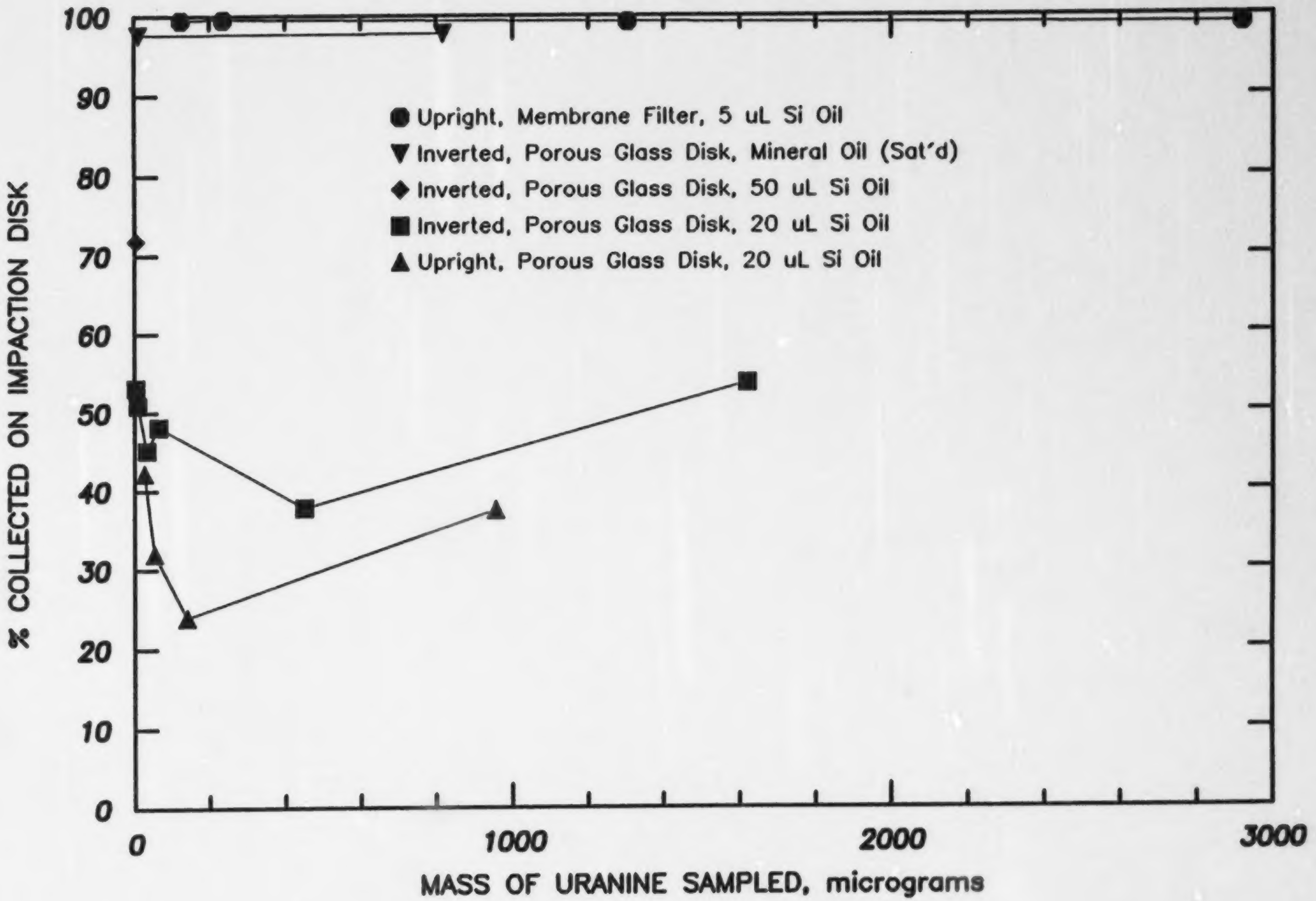

Figure 10. Impactor collection efficiency as a function of mass loading for solid 7.9-μm uranine particles.

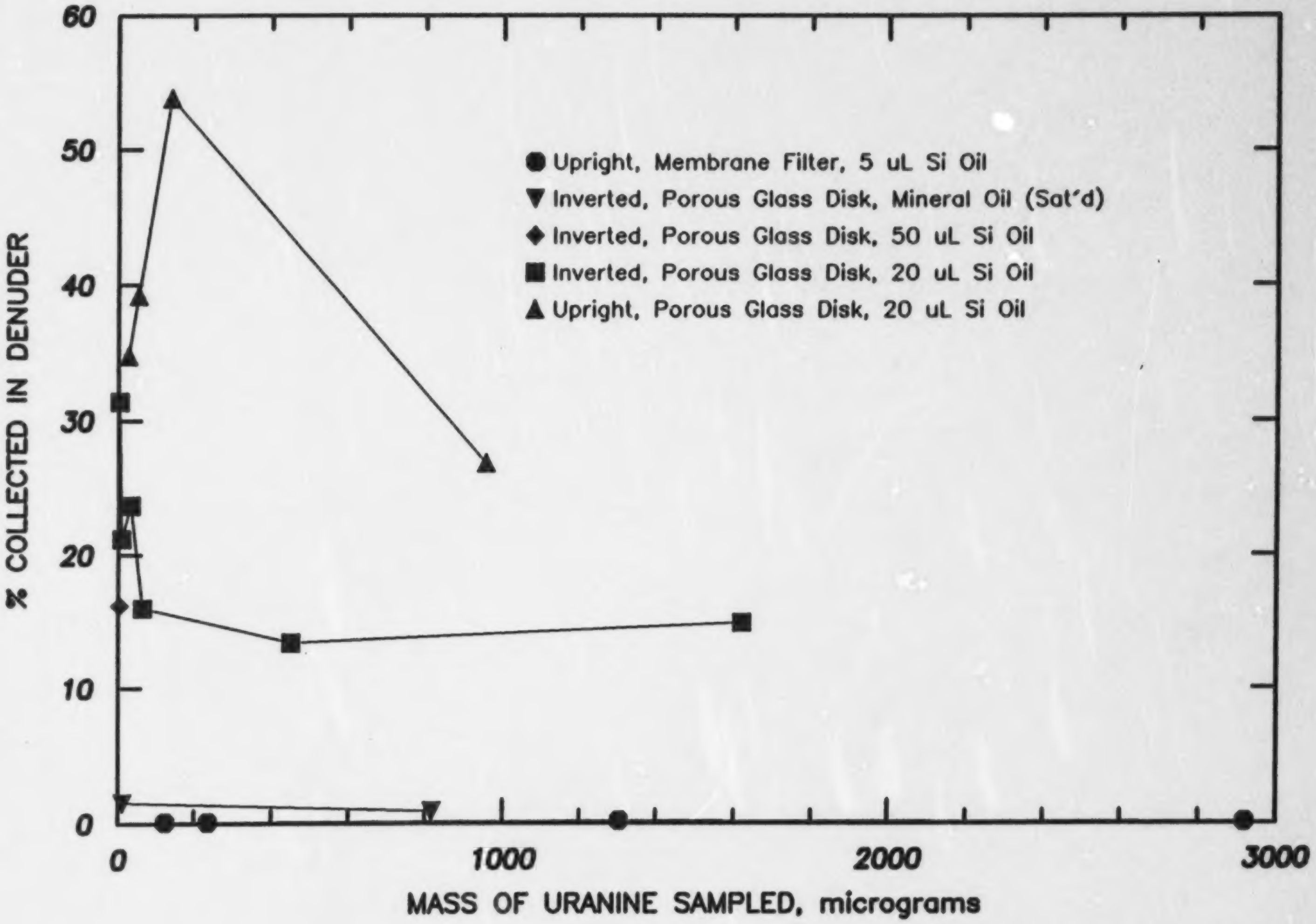

Figure 11. Denuder losses as a function of mass loading for solid 7.9-μm uranine particles.

81). Sodium-chloride particles seemed to bounce the most when collected on greased surfaces, so it was decided to compare the collection efficiencies of sodium chloride and uranine particles using oiled polycarbonate filters. As shown in Table 13, collection of sodium-chloride particles by the modified impactor, using membrane filters coated with 5 µL of silicone oil, was excellent, even at a very high mass loading (> 3 mg). The average collection efficiency for sodium chloride particles was 98.9%, only slightly less than the average of 99.3% observed for uranine particles under similar conditions (Table 12).

Oiled Porous Glass Disks

Experiments using oiled porous glass disks were run for two major reasons: 1) if lightly oiled porous glass disks were able to give a satisfactory collection efficiency, it would be possible to mount the impactors horizontally and avoid the losses associated with the inlet bend, and 2) other investigators had reported using various amounts of oil, ranging from 2 µL (200 µL of a 1% solution) to saturation, to coat porous metal or glass impaction disks (e.g., Reischl and John, 1978; John et al., 1978); but the effectiveness of such disks had not been directly compared to that of oiled polycarbonate filters. There were also questions to be answered regarding the ability of oil to wick up on an unsaturated porous disk under the force of a jet and the ability of routine extraction procedures to remove impacted particles from a porous oiled disk.

As shown in Table 14, extensive particle bounce occurred when 7.9-µm uranine particles were collected on a porous glass disk coated with 20 µL of silicone oil (200 µL of a 10% solution). This was true whether the impactors were oriented in an upright or inverted position, although the adjusted collection efficiencies were slightly higher for the inverted impactors, presumably as a result of oil flowing toward the surface of the disk under the force of gravity. The average adjusted impactor collection efficiency was a dismal 38.2%, but equally important was the fact that much of the large particle mass was collected on the denuder. Hence, large-particle bounce can interfere not only with the measurement of the fine-particle fraction but also with the determination of reactive gases using denuders.

Additional experiments sought to determine whether a lightly oiled porous glass disk could more efficiently collect particles at lower mass loadings. For porous glass disks coated with 20 µL of silicone oil (200 µL of a 10% solution in pentane) significant particle bounce was found to occur not only at mass loading approaching a monolayer (Table 15) but also at much lower mass loadings (Table 16). The latter experiment was conducted in the wind tunnel in order to see whether a greatly reduced particle loading rate would result in better performance (i.e., by giving the oil more time to wick up), but the results were dismal and only slightly better than those obtained at higher mass loadings (Tables 14 and 15). The adjusted collection efficiencies were again higher for the inverted samplers (Table 15).

Increasing the amount of oil used to coat the porous glass disks greatly improved their performance. The average adjusted collection efficiency rose to 72% using 50 µL of silicone oil (Table 17) and to 97.7% using disks saturated with mineral oil (Table 18). However, even the oil saturated disks did not perform as well as the oiled polycarbonate filters (Tables 11 through 13). Figures 10 and 11 summarize all of the results presented in this subsection of the report except those in Table 11 (membrane filters with 80 µL of oil). The oiled polycarbonate filters clearly gave the best results among the alternatives tested.

An additional problem related to the use of porous glass disks was the difficulty encountered in extracting the uranine particles from the disks. The disks were often visibly stained with uranine after they had been extracted using the normal extraction procedure. On one occasion (Table 17), more rigorous extraction of the disks (sonification for one hour, vortex mixing for 60 seconds, and sonification for another hour) produced a 14-18% increase in the total mass sampled. Oil-saturated porous glass disks were used for numerous field samples collected as part of another project, and the impaction areas were always visibly soiled following extraction of the particles. In contrast, no visible stain was ever observed on the polycarbonate filters following extraction of uranine; and the same was true for the dark-colored particles collected on oiled polycarbonate filters in the field.

E. SYSTEM PERFORMANCE VERSUS PARTICLE SIZE AND FLOWRATE

It is clear from the preceding discussion that particles greater than 5 µm (aerodynamic diameter) can be effectively collected using a properly coated impaction disk, such that they do not enter the denuder tube and filter pack. The only results for small (< 5 µm) particles heretofore presented (Table 5 and Figure 8) indicate that small particles passing the impaction disk may be deposited on the spacer, the nozzle wall, or the denuder. The following paragraphs describe several experiments examining fractional collection for particles much smaller than the cut point, for particles close to the cut point in size, for several different flowrates, and for two types of impactor nozzles.

Table 19 shows the fractional collection efficiencies observed for 0.5-µm uranine particles. On the average, only 1% of the particles were deposited in the denuder, while >98% were collected on the back-up filter. These results are in good agreement with those presented earlier (Table 5 and Figure 8) and with those of Possanzini et al. (1983), who found negligible losses in an annular denuder for particles 0.3 to 3 µm in diameter. Much smaller particles (i.e., those less than 0.3 µm in diameter) might be collected on the denuder due to their higher diffusitivity; but this possibility was not explored since this research focused on large particles.

Table 20 shows the fractional collection efficiencies observed for 0.95- to 7.9-µm uranine particles collected at flowrates ranging from 11.7 to 16.6 Lpm (STP) using two different types of nozzles (glass and aluminum). A comparison of the results of run 1 with those of run 2 and the results of runs 3 and 4 with those of run 5 indicates that denuder losses were higher at the higher flowrate, but generally less than 1% at 12.5 Lpm (STP). It was for

TABLE 19. FRACTIONAL COLLECTION OF 0.5-μm URANINE PARTICLES*

	Run 1 %	Run 2 %	Run 3 %	Avg.	Std. Dev.
Bent-Tube Inlet	0.3	0.3	0.2	0.3	0.1
Nozzle Wall	0.2	0.2	0.2	0.2	0.0
Impaction Disk	0.1	0.0	0.1	0.1	0.1
Spacer	0.2	0.4	0.2	0.3	0.1
Denuder	1.2	0.6	1.3	1.0	0.4
Back-up Filter	98.0	98.5	98.0	98.2	0.3

* Sampling rate = 11.7 Lpm (STP); sharp-edged 90° bent-tube inlets inserted into wind tunnel; porous glass disks coated with 100-130 μL of silicone-grease-saturated toluene; sampling system mounted vertically; D_{AE} = 0.5 μm.

TABLE 20. FRACTIONAL COLLECTION FOR VARIOUS PARTICLE SIZES, FLOWRATES, AND NOZZLE TYPES*

	Fractional Collection, %						
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Nozzle Type	Glass	Glass	Glass	Glass	Glass	Alum.	Alum.
Aerodynamic Diameter, μm	0.95	0.95	2.38	2.38	2.38	2.38	7.93
Sampling Rate, Lpm (STP)	12.5	16.7	11.7	11.7	16.6	12.5	16.7
Bent-Tube Inlet	0.0	0.3	0.3	0.3	0.4	0.1	0.5
Nozzle Wall	0.0	0.0	0.2	0.5	0.1	0.4	0.1
Impaction Disk	0.7	1.9	0.6	2.2	31.4	65.2	98.7
Spacer No. 1	0.5	0.3	2.5	3.5	26.2	3.5	0.1
Denuder No. 1	0.5	1.5	0.5	1.1	3.1	3.5	0.3
Spacer No. 2	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Denuder No. 2	0.0	0.0	0.3	0.3	0.5	0.2	0.1
Back-up Filter	98.3	95.9	95.6	92.1	44.2	27.1	0.2

* Impaction surfaces were membrane filters coated with 5 μL silicone oil; the sharp-edged 90° bent-tube inlets were inserted into the wind tunnel; two denuders were attached in series in a typical field-sampling configuration.

this reason that a flowrate of 12.5 Lpm was selected for many of the other experiments described in this report. A comparison of the results of runs 3 and 4 with those of run 5 indicates that the cut-point is sensitive to changes in flowrate, hence the need for the cut-point determination described in Section 8A. The results of run 5 demonstrate that a very substantial fraction of particles near the cut point in size can be deposited on the spacer at a high sampling rate (16.7 Lpm).

The PTFE/FEP-coated aluminum nozzle used in runs 6 and 7 had a removable 4.0-mm TFE jet (Section 5A). A comparison of the results of runs 3 and 4 with those of run 6 indicates that the aluminum nozzle has a significantly lower cut point (< 2.4 μm). Uranine particles were observed on the removable jet, but their mass amounted to only 0.1% of the total mass sampled. Due to the rough transition between the 10-mm inlet tube and the 4-mm jet, it was decided to determine whether larger particles would collect on the removable jet. As the results of run 7 show, 7.9-μm uranine particles did not accumulate in the nozzle; and the adjusted impactor collection efficiency was 99.2%, similar to the efficiency usually obtained using glass nozzles.

It is also worth noting that losses on the second spacer and denuder were significantly lower than those on the first spacer and denuder. This suggests that caution should be exercised in using the second denuder to obtain a "blank correction" when sampling air having high concentrations of particles and low concentrations of reactive gases.

F. PARTICLE DEPOSITION PATTERNS

Deposits of uranine particles on impaction disks were visible to the naked eye, even at low mass loadings. This was also true for particles collected in the field using sampling times as short as one hour. The particles collected from ambient air during field sampling at a rural site (Mauch et al., 1988; Randtke et al., 1989) always produced circular deposits uniformly dark in color and occupying an area approximately 3.7-mm in diameter, slightly less than the diameter of the jet and reflecting the contraction of the jet (vena contracta). This was true regardless of whether the field samples were collected using oiled porous glass disks or oiled polycarbonate filters. The deposition patterns for monodisperse particles impacted during laboratory experiments were noticeably different from those of the field samples; and the difference is attributed to the heterogeneity of the ambient aerosols with respect to their size distribution, physical properties, and chemical composition.

Uranine particles collected in a pool of oil (overlying a filter or a porous glass disk) tended to produce a somewhat dispersed pattern, presumably as a result of particle migration following impaction. For example, when 8.34-μm uranine particles were collected in an 80-μL pool of oil (Table 11), a majority of the particles were centrally located; but many clumps of particles had migrated toward the edge of the well, and some particles and a portion of the oil had even moved up onto the outer rim of the impaction disk.

Figures 12, 13, and 14 show the deposition patterns exhibited by 7.9-μm uranine particles impacted (on a polycarbonate filter coated with 5 μL of silicone oil) at three different mass loadings: 7.35, 21.5, and 89.1 μg, respectively. The pattern at the lowest mass loading (Figure 12) indicates (a bit unclearly) the presence of a double vortexing flow condition. On this occasion, the pattern was quite irregular, and the vortex was not aligned with the sharp-edged tip of the inlet (which was aligned with the mark on the edge of the impaction disk). However, on other occasions a much clearer pattern was observed; and on one occasion uranine particles impacted on an oiled porous glass disk formed a nearly perfect double vortex (i.e., a pair of helical vortices) precisely aligned with the inlet bend and strongly resembling the streamline pattern described by Pui et al. (1987) based on the work of McConalogue and Srivastava (1968). Unfortunately, photographic equipment was unavailable during the experiment, and an attempt to reproduce the pattern using a different inlet failed. The authors speculate that minor imperfections in a bent-tube inlet can result in significant distortion of the particle deposition pattern.

The authors also considered the possibility that the double-vortex deposition pattern was due, at least in part, to vortices induced in the oil film by the force of the jet. Uranine particles are relatively light and could conceivably be mobilized by floating on a film of moving oil. However, the amount of oil used was quite small, the force of the jet created a "dry" spot in the center of the oiled impaction surface (whether using a polycarbonate filter as a porous glass disk), and the double-vortex pattern was clearly observed on a lightly oiled porous glass disk on which particle movement would be expected to be difficult and incomplete. Therefore, it is believed that the double-vortex deposition pattern was the result of vortices present in the bent-tube inlet rather than vortices in the oil film.

At high mass loadings, "C-shaped" deposits were observed not only for uranine particles (Figure 14) but also for various types of monodisperse salt particles deposited onto oiled surfaces. The pattern resembled that observed by John et al. (1978) for potassium biphlthalate particles collected (without an inlet bend) on oil-soaked sintered metal plates, except that an opening in the ring of deposited particles was usually observed at high mass loadings in this study. This opening is thought to be associated with the helical vortices within the bent-tube inlet, and was expected to be aligned with the tip of the inlet. However, in this case (Figure 14) the opening in the ring at the highest mass loading was located at about a 45° angle from the sharp-edged tip of the inlet (indicated by the mark on the edge of the impaction disk).

Although Figures 12, 13, and 14 show that a majority of the uranine particles were collected in the central area of the oiled filter, some of the particles can be seen to have migrated away from this area, especially at the highest mass loading (Figure 14). This is conceivably due to particles striking the previously deposited mound of particles and bouncing "downhill" toward the sides of the disk, perhaps being entrained in a moving film of oil as well. When viewing deposits of various types of salt particles with the naked eye, only the "C-shaped" deposit could be seen; but with the aid of a dissecting microscope, clumps of particles could often be seen elsewhere on

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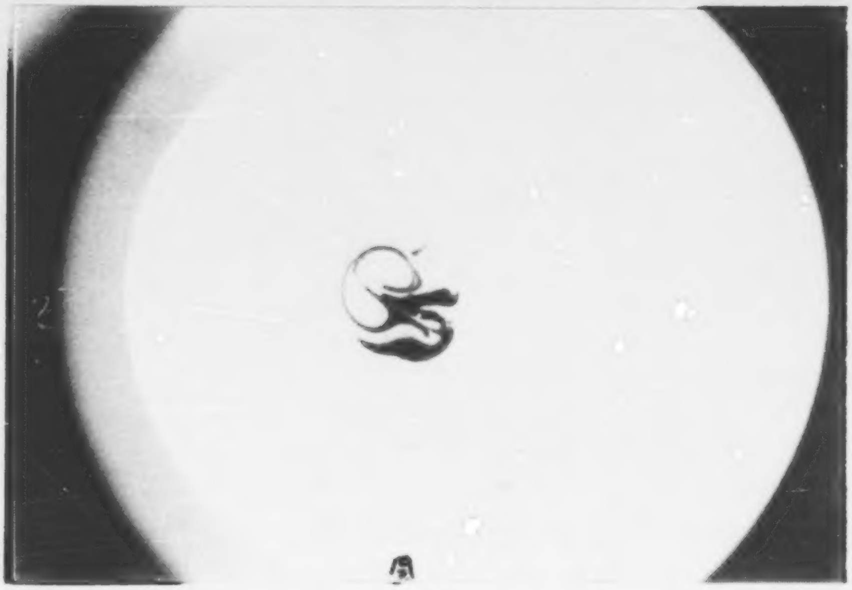

Figure 12. Deposit of 7.9-μm uranine particles at a mass loading of 7.35 μg.

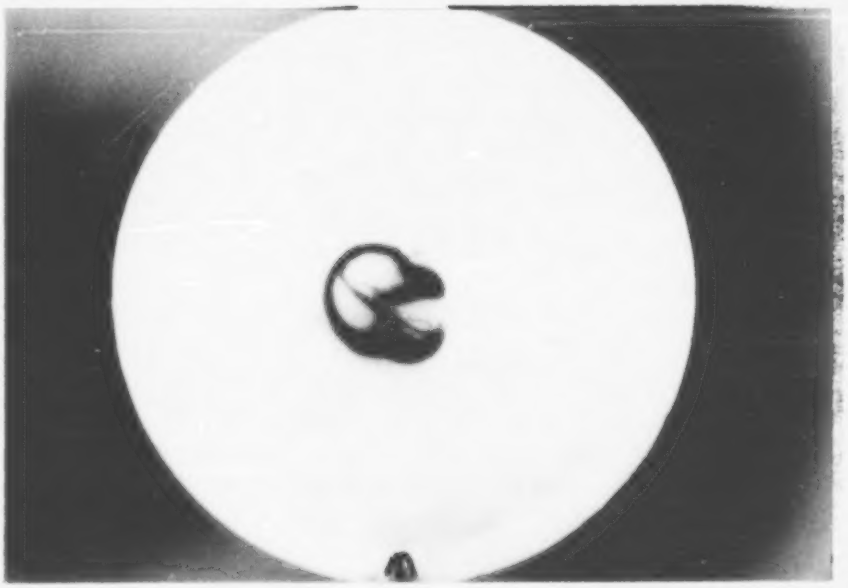

Figure 13. Deposit of 7.9-μm uranine particles at a mass loading of 21.5 μg.

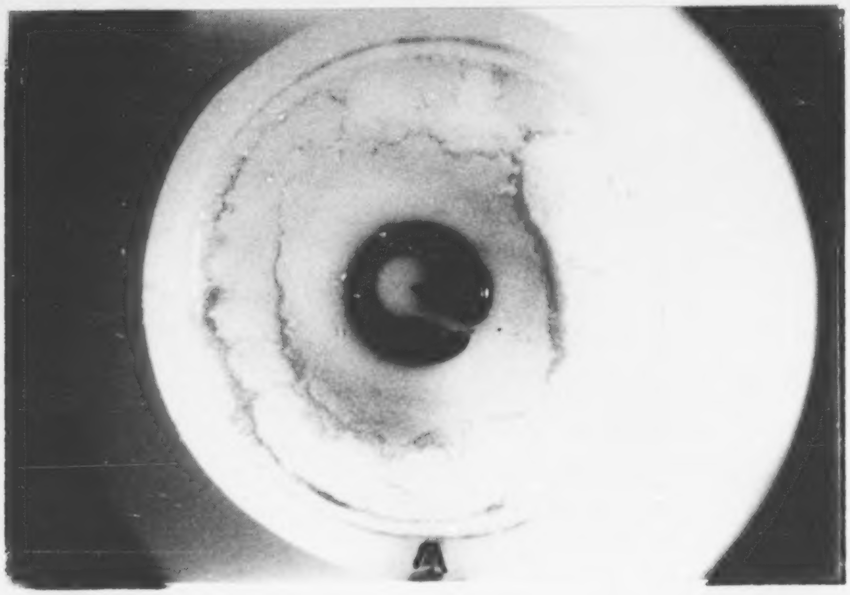

Figure 14. Deposit of 7.9-μm uranine particles at a mass loading of 89.1 μg.

the disk, especially against the rim of the disk. This was particularly true for particles impacted on greased or uncoated filters, in which case particles could sometimes be seen on the top rim of the disk as well.

Various types of monodisperse salt particles were collected under high mass loading conditions for use in experiments to examine their chemcial reactivity with various gases (Section 8I). Some types of particles seemed to "bounce" away from the center of the disk more than others. Nevertheless, the collection efficiency observed for 7.7 μm sodium-chloride particles, which seemed to bounce the most, was found to be very good (Table 13, Section 8D). On one occasion, ammonium sulfate particles collected in a pool of silicone oil stacked up so neatly, forming a hollow "C-shape" about 1-2mm high, that it was at first thought that a small shaving from the PVC pipe had fallen onto the disk.

G. SELECTION AND TESTING OF OILS AND GREASES

The problem of particle bounce has long been recognized (e.g., Dzubay _et al._, 1976); and a considerable amount of research has been done by previous investigators on the use of oils and greases to improve impactor collection efficiencies (e.g., Wesolowski _et al._, 1977; Reischl and John, 1978; John _et al._, 1978; Lawson, 1980; Williamm _et al._, 1984; Hinds _et al._, 1985; Moss &

Kenoyer, 1986). After reviewing the experiences of other researchers and considering the physical and chemical characteristics of an array of oils and greases, three oils and four greases (see Section 5B for suppliers) were selected for testing. Two common brands of mineral oil were tested, since mineral oil is inexpensive and readily available. A silicone diffusion pump oil (Dow 704) was selected for testing on the basis of its extremely low vapor pressure, its lack of aromatic hydrocarbons, and its potentially greater trace-anion purity.

Vaseline petroleum jelly was selected over other hydrocarbon greases due to its soft "sticky" nature and hence its superior potential to eliminate particle bounce (Williamson et al., 1984). Apiezon greases of various types have been used by many investigators to prevent particle bounce; but since they appeared to offer no obvious advantages over other greases and are relatively expensive, it was decided to use them only as a last resort. The Halocarbon and Fluorolube greases were selected because they are relatively non-reactive toward chemical oxidants and were considered as possible substitutes for hydrocarbon or silicone greases if these were found to react with certain gases present in ambient air. A Halocarbon grease was successfully used by Wall et al. (1988) to prevent particle bounce.

The following paragraphs describe research conducted to examine: 1) the tendency of oils and greases to leach or absorb anions; 2) the ionic purity of various oils and greases dissolved in pentane; 3) the compatibility of oils, greases, and pentane with anion analysis by IC; 4) the degree to which salt particles can be extracted from oils and greases; and 5) the gravimetric stability of silicone oil. Also, the reasons for selecting pentane as the solvent are discussed.

Leaching and Absorption of Anions

Normally, one does not associate ionic impurities with oils and greases, nor are they expected to absorb ions. Mineral oils and hydrocarbon greases are primarily composed of linear and branched hydrocarbons lacking oxygen-containing functional groups; but they may contain very small amounts of compounds having functional groups potentially able to complex ions. Silicone oils and greases could conceivably form complexes with cations or ternary complexes with anions. Because of the small concentrations of the species of interest in ambient air and the sensitivity of the analytical methods being used, leaching or absorption of even one microgram of an ion into a sample would represent gross contamination.

Oils and greases could conceivably cause an analytical interference by leaching ionic impurities into an aqueous sample, by absorbing ions from solution after the particles have been dissolved into the aqueous phase, or by absorbing ions directly from impacted particles. In the procedure described in Appendix A, the oil is dissolved in pentane prior to analysis. However, greases tend to form emulsions in pentane, rather than true solutions; oils and greases may not be completely removed from the impaction surface (especially a porous glass impaction surface); and grease may be used in other parts of the system (e.g., to seal filter packs and couplers) where it may accidentally contaminate a component (e.g., a filter or denuder) not extracted with pentane. Therefore, it was deemed appropriate to examine the leaching and absorption of anions by oils and greases in the absence of pentane.

Table 21 presents the results of a series of experiments in which oils and greases were contacted with reagent water to determine whether any anions would leach into solution. The amount of oil or grease used was 0.5 to 1.25 gms, roughly 10 to 100 times more than needed to coat an impaction disk; and the volume of water used was 10 mL, the same as was routinely used in the extraction of impaction disks. Small but significant amounts of chloride leached from the Halocarbon grease and small amounts of sulfate leached from the mineral oil. Sulfate was detected in one of three Halocarbon grease samples and one of three silicone oil samples, but was not detected when these samples were reanalyzed, which was interpreted to mean that the peaks that were detected represented baseline noise or vial contamination. The traces of chloride (< 20 µg/L) found in a number of samples could be due to sample handling rather than leaching. The Halocarbon grease consistently disrupted the early portion of the IC baseline. Overall, however, the results were very encouraging.

Tables 22 and 23 show the results obtained when 0.5- to 1.25-mg quantities of oil and grease were contacted with 100-µg/L IC standards to see if significant absorption of anions would occur within 24 hours. The vaseline and silicone grease smears were the same as those used for the earlier test (Table 21); the tubes were simply emptied, gently rinsed with 100-µg/L IC standard, then refilled with 10 mL of standard. Fresh Halocarbon smears were prepared (using approximately 500 mg of grease), because the original smears appeared to "dry out" (dessication cracks appeared to form in the smear) and the grease sloughed into the water when the original tubes were rinsed. Fresh Fluorolube smears (500 mg each) were prepared, since this grease had been received after the leaching test was completed.

A concentration of 100 µg/L was chosen for these absorption experiments for two reasons: 1) this concentration was high enough to be determined with a reasonable degree of precision and accuracy; and 2) this concentration was low enough that absorption of as little as 0.1 µg of an anion would produce a significant (10%) change in the liquid-phase concentration. As shown in Tables 22 and 23, the average measured concentrations for all seven analytes in both series of reagent blanks were within one standard deviation of the "true" value of 100 µg/L.

Although triplicate samples were analyzed in duplicate, much (if not most) of the variation was associated with the analysis itself, so the results were statistically analyzed assuming a sample size (n) of 6. For each oil or grease tested, the 95% confidence interval for each mean was determined using the following formula:

$$\begin{aligned} \text{CI (95\%)} &= \bar{\bar{Y}} \pm ts/\sqrt{n} \\ &= \bar{\bar{Y}} \pm 1.05s \text{ (for } n = 6\text{)} \end{aligned}$$

TABLE 21. CONCENTRATIONS OF ANIONS LEACHED FROM OILS AND GREASES*

Oil or Grease Tested	Samp. No.	Wt. (gms)	Concentration, µg/L Cl^-	NO_2-N	PO_4-P	Br^-	NO_3-N	SO_4^{-2}
Reagent Blank	1	---	2	ND†	ND	ND	ND	ND
	2	---	ND	ND	ND	ND	ND	ND
	3	---	ND	ND	ND	ND	ND	ND
Petroleum Jelly (Vaseline)	1	0.571	ND	ND	ND	ND	ND	ND
	2	0.909	ND	ND	ND	ND	ND	ND
	3	0.725	ND	ND	ND	ND	ND	ND
Halocarbon Grease (25-5S)	1	1.254	60‡	ND	ND	ND	ND	9
	1	1.254	70‡	ND	ND	ND	ND	ND
	2	1.050	40‡	ND	ND	ND	ND	ND
	3	0.937	60‡	ND	ND	ND	ND	ND
Fluorolube Grease (GR-290)	1	0.771	4	ND	ND	ND	ND	ND
	2	0.502	3	ND	ND	ND	ND	ND
	3	0.816	5	ND	ND	ND	ND	ND
Silicone Grease (Dow Corning high-vacuum)	1	0.522	18	ND	ND	ND	ND	ND
	2	0.688	5	ND	ND	ND	ND	ND
	3	0.610	16	ND	ND	ND	ND	ND
Silicone Oil (Dow Corning 704)	1	0.643	8	ND	ND	ND	ND	ND
	2	0.646	3	ND	ND	ND	ND	ND
	3	0.765	3	ND	ND	ND	ND	13
	3	0.765	3	ND	ND	ND	ND	ND
Mineral Oil (Fisherbrand 19)	1	0.540	12	ND	ND	ND	ND	22
	1	0.540	5	ND	ND	ND	ND	34
	2	0.696	T†	ND	ND	ND	ND	44
	2	0.696	ND	ND	ND	ND	ND	15
	3	0.750	ND	ND	ND	ND	ND	16
	3	0.750	ND	ND	ND	ND	ND	18

* The indicated amount of oil or grease was placed in a clean 15-mL polypropylene tube (greases were smeared evenly inside the tubes using a clean TFE rod); 10 mL of reagent water and 100 µL of eluant concentrate were added; and after 18 hours the water was decanted and analyzed for anions by IC. No pentane was used to dissolve the oil or grease. Samples found to contain sulfate were reanalyzed to confirm its presence.

† ND = not detected; T = trace (peak detected, but concentration <0.5 µg/L)

‡ Concentration estimated from peak height; unstable baseline caused inaccurate integration of peak area.

TABLE 22. ANION CONCENTRATIONS IN 100-µg/L STANDARDS CONTACTED WITH OILS*

		Concentration, µg/L						
Oil Tested	No.	F^-	Cl^-	NO_2-N	PO_4-P	Br^-	NO_3-N	SO_4^{-2}
Reagent Blank (no oil added)	1	98	105	101	96	103	103	88
	1	98	97	100	89	103	102	99
	2	99	104	99	99	106	100	104
	2	98	102	99	99	94	100	101
	3	101	111	99	103	103	100	109
	3	101	107	101	107	107	101	109
	Mean	99.2	104.3	99.8	98.8	102.7	101.0	101.7
	Std. Dev.	1.5	4.7	1.0	6.2	4.6	1.3	7.8
Silicone Oil (Dow Corning 704)	1	102	109	101	103	101	102	108
	1	101	103	101	98	100	101	95
	2	101	121	101	96	103	100	105
	2	102	121	101	98	104	101	105
	3	101	111	101	90	100	102	118
	3	101	104	99	97	102	101	104
	Mean	101.3†	111.5	100.7	97.0	101.7	101.2	105.8
	Std. Dev.	0.5	7.9	0.8	4.2	1.6	0.8	7.4
Mineral Oil (Fisherbrand 19)	1	107	108	100	99	102	99	124
	1	104	103	99	98	94	99	113
	2	107	106	101	93	104	100	123
	2	104	99	101	98	99	99	113
	3	102	104	99	94	99	97	129
	3	103	103	101	92	101	101	104
	Mean	104.5†	103.8	100.2	95.7	99.8	99.2	117.7†
	Std. Dev.	2.1	3.1	1.0	3.0	3.4	1.3	9.2

* A 500-mg portion of each oil was placed in each of three clean 15-mL polypropylene tubes; 10 mL of a 100-mg/L IC standard and 100 µL of eluant concentrate were added to each tube; the contents were vortex mixed for 30 seconds; and after 24 hours the standards were decanted and analyzed for anions by IC. No pentane was used to dissolve the oil. Samples were analyzed in duplicate.

† Significantly different (95% confidence, Student's t-distribution) from 100 µg/L and from the measured mean for the reagent blank.

TABLE 23. ANION CONCENTRATIONS IN 100-μg/L STANDARDS CONTACTED WITH GREASES*

Oil Tested	No.	Concentration, μg/L						
		F^-	Cl^-	NO_2-N	PO_4-P	Br^-	NO_3-N	SO_4^{-2}
Reagent Blank (no grease added)	1	99	94	98	106	108	99	99
	1	98	88	100	107	94	100	94
	2	101	94	101	88	94	99	100
	2	98	83	100	112	92	98	88
	3	108	116	101	98	95	101	109
	3	99	99	101	95	101	99	99
	Mean	100.5	95.7	100.2	101.0	97.3	99.3	98.2
	Std. Dev.	3.8	11.4	1.2	8.9	6.1	1.0	7.0
Petroleum Jelly (Vaseline)	1	101	90	99	98	96	100	91
	1	103	90	99	105	98	99	91
	2	106	93	99	102	100	99	106
	2	106	92	100	105	105	100	100
	3	105	95	99	103	105	99	100
	3	104	87	101	94	96	98	77
	Mean	104.2	91.2	99.5	101.2	100.0	99.2	94.2
	Std. Dev.	1.9	2.8	0.8	4.4	4.1	0.8	10.2
Halocarbon Grease (25-5S)	1	NR†	169	98	98	107	99	121
	1	NR	NR	NR	97	105	102	120
	2	NR	NR	NR	96	107	98	100
	2	NR	141	98	92	94	98	105
	3	NR	NR	NR	102	102	100	127
	3	NR	146	100	89	99	100	95
	Mean	--	152.0‡	98.7	95.7	102.3	99.5	111.3
	Std. Dev.	--	14.9	1.2	4.6	5.1	1.5	13.0
Fluorolube Grease (GR-290)	1	110	91	99	97	100	99	99
	1	106	85	99	97	101	99	97
	2	103	91	93	89	86	95	94
	2	104	91	97	99	98	98	99
	3	107	86	99	90	101	99	101
	3	107	91	99	92	102	96	100
	Mean	106.2‡	89.2	97.7	94.0	98.0	97.7	98.3
	Std. Dev.	2.5	2.9	2.4	4.2	6.0	1.8	2.5
Silicone Grease (Dow Corning high-vacuum)	1	101	99	98	92	103	97	94
	1	98	95	98	95	104	100	87
	2	98	99	99	95	94	99	92
	2	96	101	99	95	98	99	100
	3	93	85	96	93	100	96	97
	3	95	84	98	95	99	98	95
	Mean	96.8	93.8	98.0‡	94.2	99.7	98.2	94.2
	Std. Dev.	2.8	7.5	1.1	1.3	3.6	1.5	4.4

* See Table 22 and text for experimental details.

† NR = not resolved (baseline too unstable)

‡ Significantly different (95% confidence, Student's t-distribution) from 100 μg/L and from the measured mean for the reagent blank.

where: CI (95%) = 95% confidence interval
$\bar{Y}$ = mean concentration
t = Student's t
s = sample standard deviation

A value of Student's t of 2.571 was used for a two-tailed test with 5 degrees of freedom (Rohlf and Sokal, 1981). If the 95% CI included the "true" value of 100 µg/L, it was concluded that a statistically significant amount of absorption had not occurred.

If the 95% CI for a particular analyte did not include the value of 100 µg/L, then a second statistical test was used to determine whether the 95% CI of the difference between the measured mean of the sample and the measured mean of the reagent blank included the value of zero (i.e., to determine if the two means were significantly different). Since the two sample populations were the same size, the following formula could be used (Sokal and Ronlf, 1981):

$$\mathrm{CI}\ (95\%) = \bar{Y}_1 - \bar{Y}_2 \pm \sqrt{(s_1^2 + s_2^2)/n}$$

A value of Student's t of 2.228 was used for a two-tailed test having 10 (6 + 6 - 2) degrees of freedom.

As can be seen in Tables 22 and 23, none of the oils or greases absorbed a significant amount of any of the seven analytes tested. There was only one case (nitrite in the silicone grease samples) in which the measured mean concentration was significantly lower (statistically) than both 100 µg/L and the measured mean for the reagent blank; but the measured value of 98.0 ± 1.1 µg/L was extremely close to both values and can be attributed to a statistical anomaly (at a 95% level of confidence, one anomaly is expected to occur in every 20 samples).

In five instances a statistically significant increase in concentration was observed. Two of these were expected on the basis of earlier results (Table 21): the Halocarbon grease leached a small amount of chloride into solution (and caused baseline instability) and the mineral oil leached traces of sulfate into solution. The other three cases involved minute increases in fluoride ion; but since fluoride is not accurately determined by IC due to interference by bicarbonate ion and other early eluting anions, these results can be attributed to minor analytical interferences.

Selection of a Solvent

Preliminary (and somewhat imprecise) tests indicated that most of the particles impacted on greased surfaces appeared to dissolve into water without the use of a solvent. However, it was considered possible that particles could become trapped in some way, e.g., by becoming encapsulated in grease (especially a soft grease like Vaseline) or captured in a grease-coated pore (especially on a porous impaction surface) from which water would be excluded due to the hydrophobic nature of the grease. Furthermore, it was considered unlikely that particles could be completely extracted from oil without using a solvent to dissolve the oil; and a suitable solvent was also needed to emulsify greases for application to the impaction surface and to examine the ionic purity of the oils and greases selected for testing.

A variety of potential solvents were evaluated, including pentane, iso-octane, cyclohexane, toluene, cellosolve (ethylene glycol monoethyl ether), and a number of halogenated solvents. Pentane was selected because of: 1) its very rapid rate of evaporation (facilitating drying of impaction surfaces after coating with grease); 2) its very low aromatic hydrocarbon content (aromatic compounds, especially aromatic acids foul the IC column); 3) its very low solubility in water, as well as the very low concentration of organic carbon it left in water aerated after extraction (iso-octane and toluene left much higher amounts); 4) its high ionic purity; 5) its very low acidity (for future applications involving acid aerosols); 6) its low toxicity (safer for the technicians); 7) its ability to dissolve or form emulsions with all of the oils and greases of interest (other solvents, such as cellosolve, could not); 8) its tendency not to form stable emulsions with water (unlike toluene); and 9) its suitability for numerous future applications, such as analysis of metals or toxic organic chemicals associated with coarse particles.

Pentane was used as the primary solvent throughout this study. It was found to be totally compatible with analysis of anions by IC, and did not cause noticeable problems in any aspect of the research except that: 1) it caused warping of the polypropylene vials following prolonged exposure; and 2) it was unable to completely dissolve silicone grease and Vaseline, in both cases leaving a significant amount of small waxy particles in suspension. The first problem, which also occurred with several other solvents tested, was resolved by removing the pentane immediately from the extracted samples. Silicone grease is notoriously difficult to dissolve, and no entirely suitable solvent was identified for it. Silicone oil, on the other hand, was found to completely and quickly dissolve in pentane.

Extractable Impurities and IC Compatibility

Experiments were conducted to determine whether pentane-extractable anions were present in various oils and greases and whether standards extracted with pentane solutions of various oils and greases would still produce accurate results. Also, it was important to learn whether the aqueous extracts of such samples would interfere with the IC analysis, e.g., by causing baseline instability, by adding late eluting or co-eluting peaks, by fouling the column, etc.

The results shown in Table 24 are preliminary results that were previously published in a paper by Lane et al. (1988) describing the initial results of this research. These results are in some aspects misleading or incorrect, but they are included here for the sake of completeness, to permit the errors to be addressed, and because some of the data are pertinent to the discussion. It should be noted that very large quantities of oil and grease were used for these experiments (see the first footnote accompanying the table) and the concentrations are expressed in μg/gm of oil or grease rather

TABLE 24. RESULTS OF A PRELIMINARY ANALYSIS OF SELECTED OILS AND GREASES FOR THE PRESENCE OF ANIONIC IMPURITIES*

Oil or Grease Examined	Test No.	Type of Test†	Concentration, µg/gm			
			NO_2-N	PO_4-P	NO_3-N	Sulfate
Petroleum Jelly (Vaseline)	1	S	1.6	ND	2.0	53.2
	2		2.6	ND	ND	1.6
	3		1.0	ND	ND	ND
	4		3.0	ND	ND	0.4
Silicone Grease (Dow Corning high-vacuum)	1	S	2.4	ND	ND	>954
	3		1.0	ND	ND	118
	4		1.6	ND	ND	67.8
Mineral Oil (Duo-Seal)	1	S	0.2	ND	ND	1.8
	2		0.4	ND	ND	0.9
	3		0.2	ND	ND	0.2
	4		0.2	ND	ND	0.6
Silicone Oil (Dow Corning 704)	1	S	ND	ND	ND	2.3
	2		ND	ND	ND	1.1
	3		ND	ND	ND	ND
	4		ND	ND	ND	ND
Mineral Oil (Fisherbrand 19)	1	S	T§	ND	ND	2.3
	2		ND	ND	ND	0.8
	3		ND	ND	ND	0.8
	4		ND	ND	ND	0.7
Silicone Oil‡ (Dow Corning 704)	1	B	1.8	ND	ND	0.9
	2	B	1.7	ND	ND	0.3
	3	B	1.6	ND	ND	ND
Mineral Oil‡ (Fisherbrand 19)	1	B	1.2	ND	ND	1.7
	2	B	1.2	ND	ND	1.8
	3	B	1.2	ND	ND	1.8

* Greases were 1% emulsions in pentane, oils 10% solutions in pentane; 10 mL aliquots of pentane containing oil or grease were extracted with 20 mL of reagent water, which was then analyzed by ion chromatography.

† S = sequential (aqueous phase removed entirely after each addition of reagent water and a fresh 20 mL of water added for the next extraction); B = batch (3 aliquots of oil in pentane were extracted and analyzed separately; the reported results are the averages for 3 aliquots).

‡ Exposed to indoor (laboratory) air in a thin film (in a petri dish) for nearly 2 weeks during a weight stability study.

§ T = trace

than in µg/L. Also, the first five experiments summarized were sequential tests in which the same solution of oil or grease was repeatedly extracted with reagent water.

The nitrite data shown in Table 24 are unreliable and should be entirely disregarded. Very small nitrite peaks undoubtedly occurred during IC analysis of these samples, but a subsequent review of the raw data and the surrounding events led to the conclusion that an inadequate amount of IC eluent had been added to the samples, causing a "water dip" that resulted in the peak areas for fluoride, chloride, and nitrite being grossly overestimated by the integration procedure in use at the time. This problem was limited to a few samples analyzed in the Fall of 1987 and did not affect any other IC data included in this report.

Nitrate was found in only a single sample, undoubtedly as a result of accidental contamination; and no phosphate was found in any of the samples. These peaks would have been detected at concentrations exceeding 2 µg/L and 20 µg/L, respectively; so it is reasonable to conclude that no significant amount of phosphate or nitrate was present in any of the oils or greases included in Table 24. This includes two oils that were exposed to laboratory air in loosely covered petri dishes for nearly two weeks, indicating that these oils are very resistant to contamination and that they are probably not chemically reactive with typical indoor air pollutants.

The sulfate data in Table 24 indicate that the greases (silicone and Vaseline) were grossly contaminated with sulfate, but that the sulfate was extractable. The oils appeared to contain small amounts of sulfate. However, it is believed, on the basis of subsequent experiments, that all of the sulfate except that found in the mineral oil resulted from inadvertent contamination. The two greases had been taken from previously opened but little-used containers; and although the top layer of each grease was removed from the container and discarded, exposing supposedly virgin material, both greases somehow became contaminated with sulfate prior to or during the experiment. As discussed below, both greases (and silicone oil) were found not to contain any detectable sulfate when fresh containers were tested. It is nevertheless noteworthy that sulfate was able to be extracted from the greases, especially from Vaseline.

Table 25 presents the results of another preliminary experiment in which a 500-µg/L IC standard was extracted with hexane solutions/emulsions of several oils and greases. The silicone grease and Vaseline emulsions were preextracted with reagent water to remove sulfate. The results indicate that the oils and greases tested do not interfere with IC analysis for anion concentrations of 500 µg/L. No extraneous peaks were observed, and recovery of each analyte was reasonably close to 100%. The slightly high recoveries of sulfate may reflect slight contamination of the silicone grease and the presence of trace amounts of sulfate in the mineral oils.

Additional experiments were later conducted on various oils and greases using a 100-µg/L IC standard to increase the sensitivity of the test for interferences. Once again, the amounts of oil and grease used greatly exceeded the amounts that would be required in field sampling. The results

TABLE 25. PERCENTAGE RECOVERY OF SELECTED ANIONS FROM 400-µg/L STANDARDS EXTRACTED WITH SOLUTIONS OF OIL AND GREASE IN PENTANE*

Oil or Grease Examined†	Number of Replicates	Percentage Recovery			
		NO_2-N	PO_4-P	NO_3-N	Sulfate
Mineral Oil (Duo-Seal)	6	-	-	101±4	107±3
Mineral Oil (Fisherbrand 19)	4	106±7	104±8	104±6	115±7
Petroleum Jelly (Vaseline)	5	102±1	99±1	103±1	100±5
Silicone Grease (Dow Corning)	5	103±3	103±5	104±5	109±12

* Greases were 1% solutions and oils were 10% solutions; 20-mL portions of standards were extracted with 10-mL portions of pentane solution.

† Vaseline and silicone grease emulsions were "precleaned" by extraction with ultrapure water.

are presented in Tables 26 and 27. There were only three instances in which the mean concentration of a given analyte was statistically different from 100 µg/L and from the measured mean for the reagent blank. The mineral oil increased the sulfate concentration by over 50%, clearly indicating the presence of extractable sulfate in the oil. In the other two cases (nitrite in a pentane blank and nitrate in the mineral oil) the increase was trivial and most likely due to chance.

What these results indicate is that a variety of oils and greases are relatively pure, and when dissolved in pentane they do not interfere in the analysis of common anions by IC. The mineral oils tested contained small amounts of extractable sulfate, which might well be insignificant when using small amounts of oil to collect 24-hour samples. However, these results do not prove that extraction of salts from particles impacted on oil or grease is 100% complete. This question is addressed below.

Also shown in Table 26 are the analytical results obtained for "silicone oil dregs", the last [illegible] mL of silicone oil in a one pint-bottle that had been repeatedly used by at least five people over a period of nearly one year. The oil was still free from contamination. These data, taken together with other data presented herein (Section [illegible]) as well as numerous silicone oil blanks, including the system blanks for the field test (Section [illegible]), testify to the resistance of silicone oil to contamination by gaseous impurities present in laboratory air.

Extraction of Salt Particles from Oil and Grease

Accurate quantification of the water-soluble components of large particles impacted on oil or grease requires a method capable of

TABLE 26. PERCENTAGE RECOVERY OF SELECTED ANIONS FROM 100-µg/L STANDARDS EXTRACTED WITH SOLUTIONS OF OIL IN PENTANE*

Sample Analyzed	No.	Concentration, µg/L				
		Cl^-	NO_3-N	PO_4-P	NO_2-N	SO_4^{-2}
Standard (no pentane or oil added)	1	91	101	100	101	97
	1	9	102	98	102	97
	2	95	102	103	102	98
	2	94	104	104	104	109
	3	93	103	103	102	114
	3	94	104	106	104	101
	Mean	93.2	102.7	102.3	102.5	102.7
	Std. Dev.	1.5	1.2	2.9	1.2	7.2
Standard + Pentane (no oil added)	1	97	104	103	102	100
	1	93	104	100	103	98
	2	95	105	107	104	100
	2	95	104	103	104	97
	3	93	104	106	104	102
	3	96	105	105	105	105
	Mean	94.8	104.3†	104.0	103.7	100.3
	Std. Dev.	1.6	0.5	2.5	1.0	2.9
Silicone Oil (Dow Corning 704)	1	97	105	105	104	102
	1	96	105	105	105	105
	2	93	102	109	102	103
	2	101	104	106	103	100
	3	98	99	93	99	97
	3	100	102	99	103	106
	Mean	97.5	102.8	102.8	102.7	102.2
	Std. Dev.	2.9	2.3	5.8	2.1	3.3
Mineral Oil (Fisherbrand 10)	1	101	108	105	108	124
	1	95	106	101	108	127
	2	93	102	98	103	120
	2	95	109	98	106	121
	3	93	102	98	103	122
	3	99	108	108	105	127
	Mean	96.0	105.8	101.3	105.5†	123.5†
	Std. Dev.	3.3	3.1	4.3	2.3	3.0
Silicone Oil Blanks (only reagent water and pentane added)	1	3	ND‡	ND	ND	ND
	1	4	ND	ND	ND	ND
	2	4	ND	ND	ND	ND
	2	3	ND	ND	ND	ND

* 100 µL of oil, 10 mL of a 1000-µg/L IC standard, 100 µL of eluent concentrate, and 3 mL of pentane added to 15-mL polypropylene tubes in triplicate in the combinations shown and then vortex mixed for 30 seconds.

† Significantly different (95% confidence, Student's t-distribution) from 100 µg/L and from the measured mean for the reagent blank.

‡ ND = not detected

TABLE 27. PERCENTAGE RECOVERY OF SELECTED ANIONS FROM 100-µg/L STANDARDS EXTRACTED WITH EMULSIONS OF GREASE IN PENTANE*

Sample Analyzed	No.	Cl^-	NO_3-N	PO_4-P	NO_2-N	SO_4^{-2}
		Concentration, µg/L				
Silicone Grease	1	103	105	102	105	113
(Dow Corning high-vacuum)	1	96	103	106	104	102
	2	95	101	96	102	97
	2	106	104	104	103	102
	3	96	102	102	103	106
	3	102	105	104	104	101
	Mean	99.7	103.3	102.3	103.5	103.5
	Std. Dev.	4.6	1.6	3.4	1.0	5.5
Petroleum Jelly	1	96	103	99	103	105
(Vaseline)	1	99	104	104	104	104
	2	98	102	104	103	95
	2	102	104	100	105	98
	3	100	103	103	104	105
	3	101	105	102	104	104
	Mean	99.3	103.5	102.0	103.8	101.8
	Std. Dev.	4.3	1.0	2.1	0.8	5.0

* One mL of a 1 g/L pentane emulsion of each grease (i.e., 10 mg of grease) was added to each of three 15-mL polypropylene tubes; 10 mL of a 100-µg/L IC standard, 100 µL of eluent concentrate, and 5 mL of pentane were added, and the samples were vortex mixed for 30 seconds. Some time later the pentane layer was withdrawn, and the samples were then analyzed in duplicate for anions. The reagent blank values are shown in Table 26.

quantitatively recovering them from the oil or grease. Previous experiments conducted by the investigators indicated (but did not conclusively prove) that nitrate, sulfate, and other ions could be quantitatively recovered from grease-coated glass-fiber filter paper without the use of a solvent. Also, it seems reasonable to assume that particles impacted on a surface coated with a stiff grease such as silicone grease will not penetrate far enough into the grease to become totally encapsulated, and it is conceivable that adding a solvent to a grease-coated surface might cause the grease to coat some of the particles. Therefore, it might be better not to use a solvent to extract a grease-coated impaction surface, unless the grease is soft enough to totally envelop the impacted particles. However, because of the superior performance of silicone oil, especially at high mass loadings, the efficiency with which impacted particles could be extracted was experimentally studied only for oiled surfaces rather than greased surfaces.

To determine whether silicone oil would interfere with the extraction of sulfate from impacted particles, 8-μm ammonium-sulfate particles generated in the wind tunnel were sampled isoaxially and isokinetically and collected on: 1) oiled and unoiled PTFE filters; 2) oiled and unoiled polycarbonate (Nuclepore) filters; and 3) an oiled porous glass impaction surface. Collection, determined on the basis of extractable sulfate, was 8.3% less on the oiled PTFE filter than the unoiled PTFE filter; 10% greater on the oiled polycarbonate filter than on the unoiled polycarbonate filter; and 20% less on the oiled porous glass disk than on the unoiled PTFE filter. Since the sampling accuracy of the test was estimated to be ± 10-20%, the results only prove that the oil did not grossly interfere with extraction of sulfate.

As discussed in Section 8D, uranine particles were easily and completely extracted from oiled polycarbonate (Nuclepore) filters, as were the dark-colored deposits left on oiled polycarbonate filters during field tests. Organic matter should be more difficult to extract from an oiled filter than an ionic solid, and the pentane solutions of silicone oil clearly did not absorb anions (Table 26). Therefore, it was concluded that extraction of salts from oiled polycarbonate filters would be essentially complete. However, as discussed earlier (in Section 8D), uranine was not readily extracted from oiled porous glass impaction disks.

One concern not addressed experimentally in this study is the possible formation of ternary complexes involving silicone oil, multivalent cations, and anions. For example, it is conceivable that silicone oil could complex calcium and that this complex could in turn complex sulfate. This possibility should be examined in future research. Also, if this technique is applied to metallic constituents and hydrophobic organic compounds, it will be necessary to first demonstrate complete extraction of the species of interest.

Gravimetric Stability

In an experiment designed to assess the gravimetric stability of silicone oil and mineral oil (Fisherbrand 19), large (9-cm) plastic petri dishes were coated with about 2 mL of one oil or the other. The dishes were then loosely covered and placed in a balance room having good temperature and humidity control (21°C and 40% RH). As shown in Figure 15, the overall weight changes observed were generally less than 200 μg/gm. Such a change is negligible (less than about 1 μg) for the small amount of oil (about 5 mg) needed to coat a 13-mm membrane filter, but is potentially significant for the larger quantities of oil needed to saturate a porous glass disk. However, it is quite possible that the weight changes were associated with the petri dishes (although the tops were removed during weighing, the bottoms and sides may have attracted particles through electrostatic forces); and the day-to-day changes were generally much less than 200 μg/gm.

In a second experiment, six TFE impaction disks (Figure 3) were cleaned, dried, equilibrated in the weighing room in a large vented covered container for 24 hours, and then weighed. Two of the disks were then oiled with

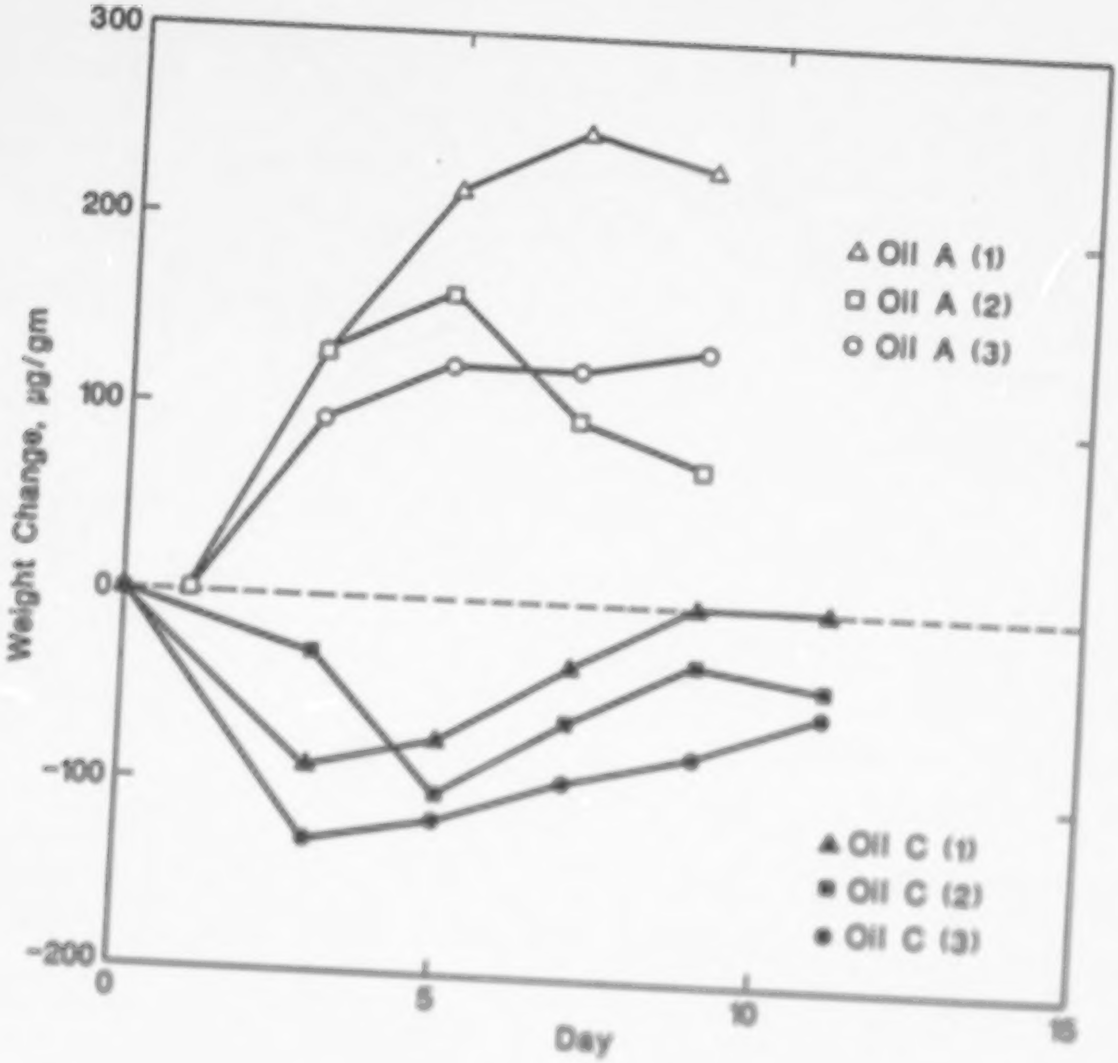

Figure 15. Gravimetric stability of mineral oil (A) and silicone oil (C).

silicone oil and two were coated with Vaseline (the latter applied in the form of a pentane emulsion). The disks were then reweighed on 10 of the next 14 days. On each day, each disk was weighed at least three times or until reproducible results were obtained. This procedure resulted in an average standard deviation of ±19 µg for 70 weighings done in triplicate. A summary of the results is presented in Table 28.

The weights of the disks decreased significantly during the first two to five days after the initial weighing, with the coated disks decreasing in weight over a longer period of time than the uncoated disks. The reason for this decrease is not clear, but possible explanations include: 1) changes in temperature and humidity (malfunction of the balance room); 2) evaporation of pentane, water, or other substances from the TFE impaction disks; and 3) loss of volatile components from the oil and Vaseline. The latter seems unlikely, especially since the uncoated (control) disks also decreased in weight.

Following the initial decrease in weight, the weights followed what at first appeared to be a rather erratic pattern, with day-to-day changes sometimes exceeding 100 µg. However, a closer inspection of the data revealed that all (10) of the large (>100 µg) weight changes after the initial decrease in weight were positive and sustained, i.e., the disks gained a significant amount of weight and did not subsequently lose it, suggesting that the disks were becoming contaminated with dust particles during the weighing process. Hence, a clean room or a dust-free glove box may be necessary to obtain reproducible results.

There were 49 weighings after the initial decrease in the weights. If the 10 weighings reflecting a large (>100 µg) weight change are ignored, the standard deviation of the weight change for the remaining 39 weighings is only 39 µg, roughly twice the precision of a single weighing and well within the accepted accuracy of such determinations. Of these 39 weight changes, 19 were positive, 19 were negative, and one was zero, indicating random variation.

A precision of ±40-50 µg is probably about the best that can be expected without heroic effort. Unfortunately, this level of precision is much too poor to permit accurate determination of large particle mass, except under very high mass loading conditions.

B. REACTIVITY OF OILS, GREASES, AND IMPACTION SURFACES

It is conceivable that gaseous constituents present in ambient air might adsorb onto or chemically react with the impaction surface, as well as any oil or grease used to coat the impaction surface, thereby leading to chemical artifact formation. Although TFE is generally quite inert, it is a relatively porous material capable of adsorbing a variety of substances; and although oils and greases are not expected to strongly adsorb onto or react with oils and greases, adsorption of even a small amount of an abundant pollutant such as SO_2, or reactions with trace impurities present in an oil or grease could significantly bias the analytical results for the coarse particle fraction.

TABLE 28. GRAVIMETRIC STABILITY OF COATED AND UNCOATED IMPACTION DISKS*

Day	Change in Weight from Previous Weighing, µg Uncoated Disk #1	Uncoated Disk #2	Oiled Disk #1	Oiled Disk #2	Greased Disk #1	Greased Disk #2
2	-250	-120	-380	-120	-190	-600
4	+ 40	- 70	-150	-70	-290	-180
5	- 30	+ 80	+ 10	+40	+ 30	-240
6	+ 50	+290	+210	+140	0	+200
7	- 20	- 30	+380	+70	+ 40	+ 50
8	+ 70	+ 50	+ 60	-20	- 30	+140
11	+ 50	+ 40	+ 50	-10	- 20	+ 20
12	+250	+ 40	- 60	-50	- 30	- 20
13	- 60	- 80	+510	+20	- 50	+ 10
14	- 60	+ 40	- 50	-10	+ 60	- 10

* The TFE impaction disks weighed between 1.8 and 1.92 gms before coating; 367 and 358 mg of silicone oil were placed on oiled disks #1 and #2, respectively; and 438 and 642 mg of Vaseline were applied to greased disks #1 and #2, respectively.

This section of the report describes a variety of simple experiments examining the extent to which nitric acid vapor (HNO_3) and sulfur dioxide (sulfurous acid) might adsorb onto or react with TFE impaction disks, filters (Nuclepore polycarbonate, Millipore cellulose acetate, and glass fiber), porous glass disks, oils (silicone and mineral oil), and greases (Vaseline and Dow high-vacuum grease). HNO_3 and SO_2 were selected because of their abundance in ambient air, their reactivity, and their potential to cause interferences. Other gases, such as NO, NO_2, HNO_2, PAN, and O_3, could potentially form artifacts and warrant investigation in future studies.

Very high concentrations of HNO_3 and SO_2, exceeding normal ambient concentrations, were used in many of the experiments. High concentrations were chosen to magnify any adsorption or chemical reaction that might occur and to produce chemical artifacts in amounts exceeding the trace levels of contamination frequently encountered in this phase of the experimental work.

However, the levels of HNO_3 and SO_2 used were not so high as to create conditions favorable for reactions that would not occur under ambient sampling conditions.

Preliminary Test Results

Prior to the design and construction of the impaction-surface exposure system described in Figure 5, a number of experiments were conducted using a similar system employing diffusion tubes (filled with HNO_3) and filters rather than scrubbers on the air intakes. The results of these experiments are summarized in Table 29. In the tests conducted "with aeration", the line from the diffusion vial was disconnected for 5-10 minutes after the desired exposure time, and the test specimen was exposed only to filtered air to provide an opportunity for any weakly adsorbed gases to desorb. On a given day, the concentration of HNO_3 in the gas stream decreased from one test run to the next, even though the system was "equilibrated" for several hours, because pressure fluctuations in the system alternately removed some concentrated nitric acid vapor from the headspace of the diffusion vial and then partially refilled the vial with relatively clean air.

A cursory examination of the data in Table 29 suggests that: 1) little if any chemical artifact formation occurred on TFE impaction discs, whether plain or oiled (immersed in silicone oil for 30 minutes and then cleaned off with a Kimwipe); 2) mixed-fiber filters (composed of cellulose acetate and cellulose nitrate) appeared to pick up about 0.3 μg of nitrate-N when exposed to high concentrations of HNO_3; 3) silicone-oiled polycarbonate filters appeared to pick up an average of 0.13 ± 0.15 μg of nitrate-N when exposed to high concentrations of HNO_3; and 4) the effect of post exposure aeration was unclear. Unfortunately, there was a great deal of variability in the data, and the concentrations of nitrate-N found on the control (unexposed) surfaces were not only above the detection limit but were very significant relative to the concentrations found on the exposed surfaces. Hence, these data should be viewed with a great deal of caution.

It should also be noted that the impaction surfaces described in Table 29 were only exposed to HNO_3 for a period of one hour. If the apparent increases in nitrate-N on the oiled filters were the result of surface adsorption (e.g., onto the TFE support disc), then similar results would be expected for a 24-hour exposure, in which case the increases would be negligible. For example, a coarse-particle nitrate-N concentration of only 0.1 μg/m³ would contribute 1.8 μg of nitrate-N to the impaction surface when sampled for 24 hours at a flowrate of 12.5 lpm. On the other hand, if the apparent increases resulted from absorption into the oil or from chemical reactions, then very significant increases might occur in a 24-hour sampling period.

In any event, the variability of these data was troubling, as were the fluctuating gas-phase concentrations of HNO_3 and the variable blank values. For this reason, considerable effort was expended to verify reagent purity, to minimize contamination of reagent blanks and system blanks, and to redesign the exposure system so that constant and controllable concentrations of HNO_3 and other gases could be produced reproducibly.

TABLE 29. RESULTS OF PRELIMINARY EXPERIMENTS TO EXAMINE CHEMICAL ARTIFACT FORMATION ON IMPACTION SURFACES[a]

Impaction Surface Studied	μg of NO_2-N Found in the Denuder		μg of NO_3^--N Found on the Impaction Surface	
	Control	Exposed	Control	Exposed
Uncoated TFE Impaction Disks				
Reagent Blank	0.00	—	0.05	—
Test Run No. 1 (with aeration)	0.26	26.7	0.08	0.12
Test Run No. 2 (with aeration)	0.20	7.32	0.08	0.08
Test Run No. 3 (with aeration)	0.16	8.17	0.07	0.08
Silicone-Oiled Mixed-Fiber Filters[b]				
Reagent Blank	0.00	—	0.35	—
Test Run No. 1 (with aeration)	0.45	700	0.31	0.41
Test Run No. 2 (with aeration)	0.38	193	0.38	0.44
Test Run No. 3 (with aeration)	0.32	91.8	0.30	0.38
Silicone-Oiled Polycarbonate Filters				
Reagent Blank	0.00	—	0.31	—
Test Run No. 1 (with aeration)	0.21	832	1.08	1.00
Test Run No. 2 (no aeration)	0.18	287	0.17	0.27
Silicone-Oiled Polycarbonate Filters				
Reagent Blank	0.17	—	0.13	—
Test Run No. 1 (no aeration)	0.30	798	0.11	0.20
Test Run No. 2 (with aeration)	0.31	108	0.18	[illegible]
Test Run No. 3 (with aeration)	0.41	126.8	[illegible]	[illegible]
Silicone-Oiled Polycarbonate Filters				
Reagent Blank	0.19	—	0.10	—
Test Run No. 1 (with aeration)	0.27	[illegible]	[illegible]	[illegible]
Test Run No. 2 (with aeration)	0.30	[illegible]	[illegible]	[illegible]
Test Run No. 3 (with aeration)	[illegible]	[illegible]	[illegible]	[illegible]
Silicone-Oiled Polycarbonate Filters on Na_2CO_3-Washed TFE Impaction Disks				
Reagent Blank	—	—	[illegible]	—
Test Run No. 1 (with aeration)	—	[illegible]	[illegible]	[illegible]
Test Run No. 2 (no aeration)	—	[illegible]	[illegible]	[illegible]
Silicone-Oiled TFE Impaction Disks (Na_2CO_3-Washed)				
Reagent Blank	[illegible]	—	[illegible]	—
Test Run No. 1 (with aeration)	—	[illegible]	—	[illegible]
Test Run No. 2 (no aeration)	—	[illegible]	—	[illegible]
Test Run No. 3 (with aeration)	—	[illegible]	—	[illegible]
Test Run No. 4 (no aeration)	—	[illegible]	—	[illegible]

[a] [illegible]

[b] [illegible]

Reagent Purity

Numerous tests and experiments were conducted to determine the source of contamination of the reagent blanks and control samples, and a number of these tests focused on reagent purity as a potential source of contamination. Table 30 shows the results obtained during one such set of tests. As on many other occasions the chemical reagents themselves were very clean when analyzed directly. The only exception was the first eluent sample extracted with pentane and silicone oil, which was assumed to be the result of an incompletely rinsed pipet (pipets were subsequently rinsed much more thoroughly prior to use). However, despite the purity of the reagents themselves, the impaction-disk reagent blanks were significantly contaminated, leading to the conclusion that contamination was being introduced during preparation, handling, and extraction of the impaction disks. As on other occasions, chloride was the only other anion observed besides nitrate and sulfate, and no interfering peaks were present.

On the basis of a number of additional tests it was concluded that:

(1) the sodium-carbonate coating reagent contained no detectable concentrations of anions other than carbonate;

(2) it made no significant difference whether the impactor tubes were dried with high-purity nitrogen, regular-grade nitrogen, zero-grade air, or compressed "air" (actually a blend of pure oxygen and nitrogen);

(3) pentane and [illegible] remained free of detectable impurities even after standing in polypropylene tubes [illegible] for periods of up to 48 hours;

(4) [illegible]

(5) [illegible]

[illegible]

[illegible]

TABLE [illegible]. RESULTS OF ONE SET OF TESTS TO EXAMINE REAGENT PURITY

Sample Description	Concentration, [illegible]		
	[illegible]	[illegible]	[illegible]
Reagent Water in a 15-mL Polypropylene Tube	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
Reagent Water + IC Eluant Concentrate			
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
Polycarbonate Filter Extracted with IC Eluant	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
IC Eluant Extracted with [illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
[illegible] Reagent Blanks[a]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]

[a] [illegible]

[illegible]

substantially, often falling below the detection limit (e.g., see the blank values reported in Section [illegible]).

The impaction-surface exposure system was carefully examined to determine whether contamination by particulate matter could occur. The inlet filters would conceivably pass submicron sized particles, but such particles would not be likely to contaminate the impaction surfaces during an experiment. Following the preliminary experiments just described, the impaction-disk exposure system was redesigned, with special attention given to elimination of foreign particles (see Section [illegible]). On one occasion, a small drop of water was observed on an impaction disk at the start of an experiment, and it was determined that the water drop had originated from a freshly cleaned [illegible]. Since a water drop could easily absorb a substantial amount of HNO_3 or NH_3, care was taken to eliminate any moisture from the system prior to all subsequent experiments.

Extra care was taken not to touch any surface that might come in contact with the samples, including filters, impaction disks, Teflon rings, and the inner surfaces of inlet tubes, end caps, and sample containers. Filters were handled with clean Teflon-coated forceps. Impaction disks were handled only with a clean [illegible]. [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] [illegible] [illegible]

[illegible]	[illegible]		
	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	--
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible] [illegible] [illegible]

[illegible]	[illegible]	[illegible]		
		[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	--	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

[illegible]

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]			
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

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[illegible]

[illegible]

significance, and potential reactivity. Particles composed of chloride salts were exposed to HNO_3, while particles composed of either chloride or nitrate salts were exposed to SO_2. Two experiments examined the reactivity of acidic $NaHSO_4$ particles with NH_3 vapor. In several experiments, impacted particles were exposed only to purified air to determine the extent to which they would volatilize.

The experimental results are presented in Tables 34 through 42. Table 43 summarizes the results and the dates on which potentially significant procedural changes were made. The results are presented in temporal order so that the effects of such changes can be more easily examined.

The first two experiments (Table 34) were designed to examine the volatility of NH_4NO_3 particles. It had been expected that they would at least partially volatilize; and, if so, it would be necessary to correct for volatilization when studying the reactivity of NH_4NO_3 particles with SO_2. Instead, it was found that no detectable amount of volatilization occurred (at 73°F and 38% RH). Since such particles have been known to volatilize from filters (e.g., Forrest et al., 1979 & 1982; Appel et al., 1981; Anlauf et al., 1986), these results were a bit surprising. It is possible that NH_4NO_3 particles simply do not volatilize when shielded from the turbulence of the air (within the boundary layer over the impaction surface). It is also possible that volatilization was prevented by high concentrations of NH_3 in the air. The inlet air was scrubbed to remove acidic gases, but not NH_3. From a citric-acid-coated denuder included in the system on 7/21/88, it was determined that the concentration of NH_3 in the air was 98 $\mu g/m^3$.

As shown in Table 35, NH_4Cl particles were also quite non-volatile (at 72-76°F and 44-53% RH), with less than 1% of the chloride migrating from the impaction surface to the denuder tube (Table 43). Less migration occurred when using oil, but the difference is not very significant due to the variability of the data and the low concentrations of chloride involved (low concentrations of chloride were not easy to accurately quantify, as noted in Section 6A). The reason for the uncharacteristically high concentrations of chloride on the impaction disk control samples of 8/3/88 and 8/4/88 is not known, but it is suspected that particles on the edge of the particle-laden disks contaminated the tool used to handle the control disks.

Table 36 presents the results of seven experiments that examined the reactivity of NH_4Cl particles with HNO_3 vapor at 72-76°F and 44-53% RH. In the tests involving uncoated impaction filters, about 25% of the particulate chloride was displaced into the denuder, and a significant amount of nitrate was deposited on the impaction disk (see Table 43). However, on a molar basis, an excessive amount of chloride was displaced in comparison to the amount of nitrate found on the disk, such that R, the ratio of the moles of displaced ion to moles of contaminant ion on the disk, was greater than unity. The excess chloride is not due to volatilization of NH_4Cl, as the NH_4-N data for these samples testify. It is quite possible that the jet dislodged some of the NH_4Cl particles from the impaction disk and deposited them in the denuder tube, and this possibility is discussed in more detail below.

TABLE 34. VOLATILITY OF IMPACTED 9.5-μm AMMONIUM-NITRATE PARTICLES EXPOSED TO AMBIENT LABORATORY AIR

Date	Sampling System Component	Nitrate-N Found, μg Without Particles	 With Particles
07/19/88	Uncoated Impaction Filter	ND*	24.05
	Na_2CO_3-Coated Denuder Tube	0.06	ND
	PTFE Filter	0.04	ND
	Nylon Filter	0.02	0.03
07/21/88	Uncoated Impaction Filter	ND	35.2
	Na_2CO_3-Coated Denuder Tube	ND	ND
	PTFE Filter	ND	ND
	Nylon Filter	ND	ND

* ND = not detected

TABLE 35. VOLATILITY OF IMPACTED 9.6-μm AMMONIUM-CHLORIDE PARTICLES EXPOSED TO AMBIENT LABORATORY AIR

Date	Sampling System Component	Chloride Found, μg Without Particles	 With Particles
08/01/88	Unoiled Impaction Filter	T*	68.79
	Na_2CO_3-Coated Denuder Tube	0.06	0.36
08/02/88	Unoiled Impaction Filter	0.02	43.50
	Na_2CO_3-Coated Denuder Tube	0.32	0.63
08/03/88	Si-Oiled Impaction Filter	9.80	118.64
	Na_2CO_3-Coated Denuder Tube	0.23	0.71
08/04/88	Si-Oiled Impaction Filter	5.80	128.60
	Na_2CO_3-Coated Denuder Tube	T	0.12

* T = trace

TABLE 36. REACTIVITY OF IMPACTED 9.6-µm-AMMONIUM-CHLORIDE PARTICLES EXPOSED TO HNO_3 VAPOR*

Date	Sampling System Component	Nitrate-N Found, µg		Chloride Found, µg		Ammonium-N Found, µg	
		Without Particles	With Particles	Without Particles	With Particles	Without Particles	With Particles
08/01/88	Uncoated Impaction Filter	0.84	3.41	0.36	29.82	--	--
	Na_2CO_3-Coated Denuder Tube	325	298	0.21	11.53	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.00	0.00
08/02/88	Uncoated Impaction Filter	0.22	3.35	0.07	43.40	--	--
	Na_2CO_3-Coated Denuder Tube	315	280	0.31	14.50	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.80	0.70
08/03/88	Si-Oiled Impaction Filter	0.20	0.37	T	84.29	--	--
	Na_2CO_3-Coated Denuder Tube	308	282	0.26	1.58	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.00	0.00
08/04/88	Si-Oiled Impaction Filter	0.90	1.38	0.91	68.38	--	--
	·Na_2CO_3-Coated Denuder Tube	292	267	T	2.26	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	3.30	3.50
08/05/88	Si-Oiled Impaction Filter	<RB	<RB	T	48.57	--	--
	Na_2CO_3-Coated Denuder Tube	290	305	0.64	1.06	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.00	2.00
08/09/88	Si-Greased Impaction Filter	0.19	1.12	T	19.94	--	--
	Na_2CO_3-Coated Denuder Tube	285	291	0.66	35.92	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.45	0.65
08/09/88	Si-Greased Impaction Filter	0.21	3.09	0.52	11.15	--	--
	Na_2CO_3-Coated Denuder Tube	416	98.6	0.54	11.03	--	--
	Citric-Acid-Coated Denuder	NA	NA	NA	NA	0.25	8.05

* Samples were aerated with HNO_3-free air for 5-10 minutes after exposure to HNO_3, except on 8/3/88 and 8/9/88. NA = Not applicable; T = trace; and <RB = concentration less than that of the reagent blank.

TABLE 37. REACTIVITY OF IMPACTED 9.4-μm SODIUM-CHLORIDE PARTICLES EXPOSED TO HNO_3 VAPOR

Date	Sampling System Component	Nitrate-N Found, μg		Chloride Found, μg	
		Without Particles	With Particles	Without Particles	With Particles
08/12/88	Uncoated Impaction Filter	0.18	1.75	0.27	9.22
	Na_2CO_3-Coated Denuder Tube	301	302	0.29	7.31
08/15/88	Si-Oiled Impaction Filter	0.20	0.92	0.15	52.62
	TFE Impaction Disk	--	0.27	--	37.38
	Na_2CO_3-Coated Denuder Tube	306	301	0.35	2.43
08/16/88	Si-Greased Impaction Filter	0.22	2.38	0.12	23.88
	TFE Impaction Disk	0.09	0.76	0.33	19.45
	Na_2CO_3-Coated Denuder Tube	255	282	0.62	8.09
08/19/88	Si-Oiled Impaction Filter*	0.23	3.31	1.53	144.81
	TFE Impaction Disk	0.10	0.12	0.45	1.05
	Na_2CO_3-Coated Denuder Tube	273	268	2.70	11.37
08/22/88	Si-Oiled Impaction Filter	0.19	2.74	0.12	105.31
	TFE Impaction Disk	0.06	0.45	0.16	131.33
	Na_2CO_3-Coated Denuder Tube	308	270	2.01	8.56
08/31/88	Si-Oiled Impaction Filter*	0.11	0.14	0.10	6.57
	TFE Impaction Disk	0.08	0.08	0.09	0.13
	Na_2CO_3-Coated Denuder Tube	27.29	26.73	0.66	0.16
09/07/88	Si-Oiled Impaction Filter	0.15	0.25	0.33	25.26
	TFE Impaction Disk	0.14	0.12	0.53	0.40
	Na_2CO_3-Coated Denuder Tube	51.60	53.30	0.78	1.04
09/14/88	Si-Oiled Impaction Filter	0.10	0.20	T†	35.75
	TFE Impaction Disk	0.07	0.08	T	T
	Na_2CO_3-Coated Denuder Tube	63.42	63.05	0.06	0.27
09/21/88	Si-Oiled Impaction Filter	0.09	0.32	0.09	57.08
	TFE Impaction Disk	0.05	0.08	0.12	0.15
	Na_2CO_3-Coated Denuder Tube	51.56	51.45	0.75	1.48

* Only two μL of silicone oil were used instead of five.

† T = trace

TABLE 38. REACTIVITY AND VOLATILITY OF IMPACTED 9.5-µm AMMONIUM-NITRATE PARTICLES EXPOSED TO SO_2 VAPOR AND PURIFIED AIR, RESPECTIVELY*

		Nitrate-N Found, µg		Sulfate Found, µg	
Date	Sampling System Component	Without Particles	With Particles	Without Particles	With Particles
09/30/88	Si-Oiled Impaction Filter	0.13	34.92	0.12	0.23
	TFE Impaction Disk	0.08	0.07	0.13	0.13
	Na_2CO_3-Coated Denuder Tube	3.14	3.08	370.9	371.1
10/03/88	Uncoated Impaction Filter	0.26	3.47	0.62	0.12
	TFE Impaction Disk	0.13	0.05	0.29	0.13
	Na_2CO_3-Coated Denuder Tube	2.30	2.19	343.5	336.8
10/07/88	Uncoated Impaction Filter	0.05	48.72	0.25	0.14
	TFE Impaction Disk	0.04	0.06	0.14	0.12
	Na_2CO_3-Coated Denuder Tube	2.21	2.54	483.6	486.4
10/07/88†	Uncoated Impaction Filter	0.03	52.17	0.16	0.36
	TFE Impaction Disk	0.09	0.06	0.14	0.12
	Na_2CO_3-Coated Denuder Tube	0.09	0.15	0.15	0.13

* A fresh citric-acid-coated denuder was used to remove NH_3 from the inlet air.

† On this date, the sample was exposed only to air (passed through a lime-soda scrubber) to examine the volatility of the NH_4NO_3 particles. Citric-acid-coated denuder tubes were included; but the mass of ammonia found on the particle side was less than was found on the control side.

TABLE 39. REACTIVITY AND VOLATILITY OF IMPACTED 9.6-μm AMMONIUM-CHLORIDE PARTICLES EXPOSED TO SO_2 VAPOR AND PURIFIED AIR, RESPECTIVELY*

		Chloride Found, μg		Sulfate Found, μg	
Vapor	Sampling System Component	Without Particles	With Particles	Without Particles	With Particles
SO_2	Uncoated Impaction Filter	1.08	47.20	0.32	0.26
	TFE Impaction Disk	1.15	2.18	0.18	0.21
	Na_2CO_3-Coated Denuder Tube	1.08	3.58	460.1	452.0
Air Only†	Uncoated Impaction Filter	1.04	28.41	0.30	0.23
	TFE Impaction Disk	1.35	1.43	0.33	0.22
	Na_2CO_3-Coated Denuder Tube	0.20	1.31	0.27	0.37

* Experiments run on 10/12/88; nitrate was also measured, but the concentrations of nitrate on the impaction filters "with particles" were the same as those on the controls.

† In the "air only" experiment, citric-acid-coated denuders downstream of the impaction disk were analyzed for ammonium; the concentration of ammonium for the "with particles" sample was less than for the control sample.

TABLE 40. REACTIVITY OF 9.4-μm SODIUM-CHLORIDE PARTICLES IMPACTED ON SILICONE GREASE AND EXPOSED TO SO_2 AND HNO_3 VAPOR*

		Chloride Found, μg		Sulfate Found, μg	
Vapor	Sampling System Component	Without Particles	With Particles	Without Particles	With Particles
SO_2	Si-Greased Impaction Filter	0.23	95.62	0.15	0.11
	TFE Impaction Disk	0.45	0.75	0.15	0.18
	Na_2CO_3-Coated Denuder Tube	0.66	1.14	374.6	375.3
				Nitrate-N Found, μg	
HNO_3	Si-Greased Impaction Filter	1.06	124.32	0.10	0.44
	TFE Impaction Disk	7.20	1.06	0.07	0.07
	Na_2CO_3-Coated Denuder Tube	1.45	2.02	89.11	89.44
HNO_3	Si-Greased Impaction Filter	1.20	113.36	0.11	0.84
	TFE Impaction Disk	0.43	0.69	0.10	0.06
	Na_2CO_3-Coated Denuder Tube	1.72	3.27	107.00	104.16

* Experiments run between 10/21/88 and 11/4/88.

TABLE 41. REACTIVITY OF 9.6-μm AMMONIUM-CHLORIDE PARTICLES IMPACTED ON SILICONE GREASE AND EXPOSED TO HNO_3 VAPOR*

		Chloride Found, μg		Nitrate-N Found, μg	
Date	Sampling System Component	Without Particles	With Particles	Without Particles	With Particles
11/11/88	Si-Greased Impaction Filter	0.35	43.48	0.12	1.47
	TFE Impaction Disk	0.23	1.01	0.07	0.20
	Na_2CO_3-Coated Denuder Tube	1.43	5.00	124.19	122.28
11/18/88	Si-Greased Impaction Filter	0.54	106.63	0.08	0.98
	TFE Impaction Disk	0.04	1.21	0.04	0.20
	Na_2CO_3-Coated Denuder Tube	3.64	1.48	109.87	110.04

* The concentrations of ammonium-N found on the citric-acid-coated denuder tubes were the same in the test samples and control samples.

TABLE 42. REACTIVITY OF 10.0-μm SODIUM-BISULFATE PARTICLES IMPACTED ON SILICONE GREASE AND EXPOSED TO NH_3 VAPOR

		Sulfate Found, μg		Ammonium-N Found, μg	
Date	Sampling System Component	Without Particles	With Particles	Without Particles	With Particles
11/25/88	Si-Greased Impaction Filter	ND	369.59	0.20	2.10
	TFE Impaction Disk	0.11	ND	0.20	0.20
	Na_2CO_3-Coated Denuder Tube	0.33	0.27	--	--
	Citric-Acid-Coated Denuder	--	--	279.2	129.2
12/01/88	Si-Greased Impaction Filter	0.27	396.06	0.50	1.50
	TFE Impaction Disk	0.16	0.13	0.60	0.60
	Na_2CO_3-Coated Denuder Tube	0.79	0.43	--	--
	Citric-Acid-Coated Denuder	--	--	374.0	374.0

TABLE 43. SUMMARY OF PARTICLE VOLATILITY AND REACTIVITY EXPERIMENTS*

Date	Particle	Particle	Oil or	Test Gas		Mass Found	Displacement to Denuder		
(1988)	Type	Mass, µg	Grease	Type	µg/m³	on Disk, µg	Ion	%	R
7/19	NH_4NO_3	137.4	None	Air	---	NA†	Nitrate	0.00	NA
7/21	NH_4NO_3	201.3	None	Air	---	NA	Nitrate	0.00	NA
8/01	NH_4Cl	104.4	None	Air	---	NA	Chloride	0.43	NA
8/02	NH_4Cl	66.2	None	Air	---	NA	Chloride	0.71	NA
8/03	NH_4Cl	180.0	Oil	Air	---	NA	Chloride	0.40	NA
8/04	NH_4Cl	194.6	Oil	Air	---	NA	Chloride	0.09	NA
8/01	NH_4Cl	62.2	None	HNO_3	338	2.57(NO_3-N)	Chloride	27.5	1.74
8/02	NH_4Cl	87.0	None	HNO_3	318	3.13(NO_3-N)	Chloride	24.6	1.79
8/03	NH_4Cl	129.4	Oil	HNO_3	317	0.17(NO_3-N)	Chloride	1.5	3.10
8/04	NH_4Cl	106.8	Oil	HNO_3	301	0.48(NO_3-N)	Chloride	3.2	1.86
8/05	NH_4Cl	74.0	Oil	HNO_3	343	0.00(NO_3-N)	Chloride	0.9	--
8/06	After this date, samples were no longer aerated following exposure to the test gas.								
8/09	NH_4Cl	83.4	Grease	HNO_3	328	0.93(NO_3-N)	Chloride	63.9	15.07
8/09	NH_4Cl	32.7	Grease	HNO_3	114	2.88(NO_3-N)	Chloride	48.5	1.44
8/12	NaCl	26.8	None	HNO_3	341	1.57(NO_3-N)	Chloride	43.2	1.77
8/15	NaCl	148.4	Oil	HNO_3	340	0.72(NO_3-N)	Chloride	2.3	1.14
8/16	NaCl	70.9	Grease	HNO_3	320	2.83(NO_3-N)	Chloride	14.7	1.04
8/18	After this date, impacted particles were transferred to a fresh TFE impaction disk prior to exposure.								
8/19	NaCl	239.7	Oil‡	HNO_3	304	3.08(NO_3-N)	Chloride	5.6	1.11
8/22	NaCl	389.8	Oil	HNO_3	307	2.94(NO_3-N)	Chloride	2.7	0.88

* Particle mass = mass found on impaction disk plus net (corrected) mass found on denuder; oil = 5 µL of silicone oil, except where otherwise indicated; gas concentrations are reported in µg/m³ as nitric acid or as sulfate, based on the nominal flowrate and corrected mass of the relevant ion found on the exposed side of the system; "mass found on disk" is the net (control-corrected) mass of contaminant found on the impaction filter and disk following exposure to the test gas; "displacement to denuder" refers to the movement of anions from the impaction disk to the denuder due to volatilization or reaction with the test gas; R is the control-corrected ratio of moles of ion displaced to moles of contaminant ion found on the impaction filter.

† NA = not applicable

‡ Only 2 µL of silicone oil were used to coat the impaction surface.

TABLE 43. SUMMARY OF PARTICLE VOLATILITY AND REACTIVITY EXPERIMENTS (Cont'd)

Date	Particle	Particle	Oil or	Test Gas		Mass Found	Displacement to Denuder		
(1988)	Type	Mass, µg	Grease	Type	µg/m³	on Disk, µg	Ion	%	R
8/23	After this date, the "soft start" procedure was used.								
8/31	$NaCl$	10.9	Oil†	HNO_3	30.1	0.03(NO_3-N)	Chloride	0.00	0.00
9/07	$NaCl$	41.6	Oil	HNO_3	60.0	0.10(NO_3-N)	Chloride	1.0	1.03
9/14	$NaCl$	58.9	Oil	HNO_3	71.0	0.11(NO_3-N)	Chloride	0.58	0.93
9/21	$NaCl$	94.1	Oil	HNO_3	58.1	0.26(NO_3-N)	Chloride	1.3	1.11
9/28	After this date, a fresh citric-acid-coated denuder was used to scrub the inlet air when N-containing particles were exposed.								
9/30	NH_4NO_3	199.9	Oil	SO_2	371	0.11(SO_4)	Nitrate	0.00	0.00
10/03	NH_4NO_3	20.1	None	SO_2	337	0.00(SO_4)	Nitrate	0.00	--
10/07	NH_4NO_3	208.6	None	SO_2	486	0.00(SO_4)	Nitrate	0.67	--
10/07	NH_4NO_3	298.8	None	Air	---	NA	Nitrate	0.11	NA
10/12	NH_4Cl	78.4	None	SO_2	452	0.00(SO_4)	Chloride	4.8	--
10/12	NH_4Cl	46.8	None	Air	---	NA	Chloride	3.6	NA
10/21	$NaCl$	159.7	Grease	SO_2	375	0.00(SO_4)	Chloride	0.50	--
10/28	$NaCl$	207.6	Grease	HNO_3	101	0.33(NO_3-N)	Chloride	0.45	0.66
11/04	$NaCl$	190.6	Grease	HNO_3	118	0.73(NO_3-N)	Chloride	1.34	0.34
11/11	NH_4Cl	72.6	Grease	HNO_3	139	1.48(NO_3-N)	Chloride	7.43	0.96
11/18	NH_4Cl	163.0	Grease	HNO_3	125	1.06(NO_3-N)	Chloride	0.00	0.00
11/25	$NaHSO_4$	461.9	Grease	NH_3	39.8	1.90(NH_4-N)	(3.5% conversion)**		
12/01	$NaHSO_4$	495.0	Grease	NH_3	114	1.00(NH_4-N)	(1.7% conversion)**		

† Only 2 µL of silicone oil were used to coat the impaction surface.

** Assuming that the ammonia was converted to ammonium sulfate.

When NH_4Cl particles were impacted on a silicone-oil-coated filter, very little reaction with HNO_3 occurred, and only 1-3% of the chloride initially present migrated into the denuder (Tables 36 and 43). This indicates that the oil prevented either the reaction or the dislodging of the particles, or both. The extent of reaction, if real, is quite small in view of the large mass of particles present and the high concentrations of HNO_3 to which they were exposed.

In experiments conducted on 8/1/88 through 8/4/88, an unusually high concentration of nitrite was found in the denuder on the side of the system containing the particles. At first it was thought that this might be due to a reaction of HNO_3 with the NH_4Cl particles, but a small brass fitting was subsequently found connected to one of the TFE sleeves. Although only about a quarter of an inch of brass was exposed, about 1% of the HNO_3 was found on the denuder as nitrite. The brass fitting was immediately replaced with a stainless steel fitting, which did not react catalytically with HNO_3.

The results of the last two experiments presented in Table 36 show that a very substantial percentage (48-64%) of the particulate chloride migrated into the denuder tube when the particles were impacted on a silicone-greased surface. Whether the particles were blown off or reacted with the HNO_3 is not clear; but in any event a significant amount of nitrate was found on the impaction disk. Oil clearly gave the best results.

Table 37 presents the results of nine experiments that examined the reactivity of NaCl particles with HNO_3 vapor at 69-73°F and 34-48% RH. Although NaCl particles are typically abundant only in coastal and marine areas, they were selected for testing because they are non-volatile and because if they were reactive they would help to examine differences among various impaction surface coatings.

The results of the first three experiments described in Table 37 indicate that the performance of the oiled filter exceeded that of both the uncoated filter and the greased filter. Without oil, much more particulate chloride was displaced into the denuder and significantly greater amounts of nitrate were found on the impaction disk (see Table 43). It is possible that some NaCl particles were dislodged into the denuder at the start of the experiment (when the bypass valve was suddenly turned), but this does not explain the presence of nitrate on the impaction filter. Note that in each case a large percentage of the particle mass (chloride) was found on the TFE impaction disk rather than on the impaction filter, suggesting that the particles were not being deposited or were not remaining in the intended location.

On 8/18/88, a dissecting microscope was set up to examine the particle deposits on uncoated and oiled filters. On one TFE impaction disk fitted with an uncoated filter, a majority of the NaCl particles were found along the edge of the disk and up on the rim. (As noted in Section 8F, NaCl particles appeared to bounce more so than other types of particles.) NaCl particles impacted on oiled filters were concentrated in the center of the impaction filter, and no particles could be observed on or near the rim of the TFE disk. Because particles on the rim of the impaction disk might be much more reactive than those in the center of the impaction filter, it was decided to circumvent this possibility by moving the filter (with particles) to a clean TFE impaction disk prior to exposing the particles to the test gas. This procedural change was implemented on 8/19/88 and continued throughout the remainder of the experiments.

On 8/18/88, NaCl particles were impacted on membrane filters coated with either two or five µL of silicone oil. The filters were removed from the TFE impaction disks for analysis, and the wells of both disks were then rinsed with reagent water, which was subsequently analyzed. The well that had held the filter coated with two µL of silicone oil was found to contain 2.2% of the impacted mass, while the well that had held the filter coated with five µL of silicone oil contained only 0.4% of the impacted mass. In both cases the total impacted mass was about 158 µg. It therefore appears that using five µL of oil rather than two µL of oil more effectively prevents migration of the particles to the edge of the well under high mass loading conditions.

On 8/19/88 and 8/22/88, NaCl particles impacted on filters coated with two and five µL of silicone oil, respectively, were exposed to HNO_3 (Tables 37 and 43). Better results were obtained using the larger quantity of oil. In both cases measurable amounts of particulate chloride, representing 2.7 to 5.6% of the initial mass of chloride present, migrated from the impaction disk to the denuder; and a roughly equivalent amount of nitrate was deposited on the impaction disk, clearly indicating the occurrence of a metathetical reaction. Note, however, that very large masses of particles and very high concentrations of HNO_3 were present. Also, on 8/22/88, a large mass of chloride was found on the TFE disk, even though the particles had been transferred to a clean disk after impaction. Apparently, particles were moving from the filter to the disk during exposure to the test gas.

On 8/23/88, the effects of sudden changes in flowrate on particle deposits were examined. Deposits of NaCl particles were observed to be unaffected by the jet when the flowrate was increased gradually up to 16.7 Lpm, but when suddenly exposed to the full force of the jet, some of the particles were clearly displaced, even in the presence of oil. In the absence of oil (i.e., when using uncoated or greased filters), particles may be dislodged from the disk and contaminate other components of the sampling system. Oil may prevent dislodging of the particles, but particles were still observed to migrate away from the center of the oiled impaction area under the force of the jet. Migration of particles on the oiled filter was attributed to a procedural artifact, since stopping the flow allowed the oil film to flow back into the deposited particles, creating conditions conducive to particle migration. Under continuous flow, the oil film is continuously pushed aside while the particles are deposited, but any interuption in flow could cause the particles to migrate when flow is resumed.

To avoid dislodging particles from the filter onto the disk or into the denuder in subsequent experiments, a "soft start" procedure was implemented on 8/23/88. Before switching the bypass valve, the flow was turned off using the flow controller and then gradually turned up to 16.7 Lpm to begin the experiment. After this change was made, very little particle mass was found on the TFE impaction disks (see Tables 37 through 42); and the particles appeared to remain in place on the impaction filter.

In four additional experiments involving NaCl particles impacted on oiled filters and exposed to HNO_3 (Table 37), very little of the chloride (0.0 to 1.3%) was displaced into the denuder; and only small amounts of nitrate were found on the impaction disk (mostly on the filter). The particle masses and HNO_3 concentrations were substantially lower than those used in earlier experiments (8/19/88 and 8/22/88).

Table 38 presents the results of several experiments designed to examine the reactivity and volatility of NH_4NO_3 particles exposed to SO_2 and air, respectively, at 70-78°F and 28-43% RH. No significant reaction or volatilization occurred, even when the impaction surface was greased rather than oiled. Only an insignificant trace of nitrate was found on the denuder, even though a citric-acid-coated denuder tube removed NH_3 from the incoming air (in contrast to the experiments addressed in Table 34). Hence, impacted NH_4NO_3 particles appear to be relatively non-volatile even in the absence of HNO_3 and NH_3.

Table 39 presents the results of two experiments designed to examine the reactivity and volatility of NH_4Cl particles exposed to SO_2 and air, respectively, at 80°F and 23% RH. The inlet air was scrubbed to remove both acidic gases and NH_3. A small amount of chloride (3.6 to 4.8%) appeared to volatilize, but the particles did not react with sulfate (see Table 43).

During preparation of the particle-laden disks for the experiments described in Table 39, microscopic examination revealed that particles were being deposited only on the area of the uncoated filters underlain by the small dab of silicone grease. Presumably, particles deposited on other areas of the filter were simply bouncing off. Therefore, in all subsequent experiments, greased rather than uncoated filters were used. Oiled filters were not used because the intent at this time was to identify significant reactions, so that later experiments could examine the effectiveness of oil in preventing reactions between particles and gases.

Table 40 presents the results of three experiments designed to examine the reactivity of NaCl particles with HNO_3 and SO_2 at 67-81°F and 19-36% RH. The particles, which were impacted on silicone-greased surfaces, did not react with SO_2; but a small amount of chloride appeared to be displaced by the HNO_3, which also left measurable amounts of nitrate on the impaction filters (also see Table 43).

Table 41 presents the results of two experiments designed to examine the reactivity of NH_4Cl particles exposed to HNO_3 vapor at 75°F and 22% RH. In both cases, a measurable amount of nitrate was deposited on the impaction surface, but chloride was found to be displaced only in the first experiment. In the second experiment, it is assumed that the control denuder became contaminated with chloride.

Table 42 presents the results of two experiments designed to examine the reactivity of acidic $NaHSO_4$ particles with NH_3 (a base) at 74°F and 23-25% RH. No displacement was expected in this case, since the reaction of NH_3 with $NaHSO_4$ is expected to produce $NaNH_4SO_4$. A small but measurable amount of ammonium nitrogen was found on the impaction filters, indicating that 1.7 to 3.5% of the $NaHSO_4$ was converted to $NaNH_4SO_4$.

In summary, NH_4NO_3 and NH_4Cl particles were relatively non-volatile under the conditions tested. Chloride-containing particles reacted to a limited extent with HNO_3 but not with SO_2; and nitrate containing particles did not react to a significant extent with SO_2. Oil appeared to reduce particle reactivity, and it clearly produced better results than grease when sudden changes in flow occurred. Above all, these results testify to the suitability of this sampling system for large nitrogen- and sulfur-bearing aerosols, including acidic aerosols, in the presence of reactive gases.

J. FIELD TEST RESULTS

A 24-hour field test employing four collocated sampling systems was conducted as described in Section 7E and Appendix A. Anion concentrations were accurately determined by analyzing five replicates of each sample (except the Nylon-filter samples, which caused baseline instability after a short time), while ammonium concentrations were determined in duplicate and averaged. The results, which include blank corrections, are presented in Table 44. The fine-particle nitrate concentrations were not corrected for volatilization (the nitrate captured on the Nylon filters) because the citric-acid-coated glass-fiber filters had lower ammonium concentrations than the blanks and because the nitrate concentrations on the Nylon filters were erratic.

The precision of the method for total coarse-particle nitrate-N, sulfate, and ammonium-N was found to be 3.4%, 3.3%, and 10.4%, respectively, for ambient concentrations of 0.21, 0.22, and 0.10 $\mu g/m^3$, respectively. Such precision is excellent for the very low ambient concentrations measured. The precision was better than ± 5% for the fine-particle constituents, 2.9% for SO_2, and a relatively poor 7.0% for nitric acid. These results are comparable with those of Stevens et al. (1988a & 1988b) and Vossler et al. (1988), significantly better than those reported by Anlauf et al. (1986), and well within the ± 10-20% generally considered to be reasonable for monitoring activities (e.g., Sickles et al., 1987).

Examination of the coarse particle data in Table 44 revealed a potentially significant problem. Thirty-six percent of the nitrate, 44% of the sulfate, and 50% of the ammonium was found in the bent-tube inlet. These amounts were included with the coarse-particle fraction based on the assumption that the constituents originated from very coarse (> 10 µm) or very sticky particles rather than from adsorption of reactive gases onto the inlet or onto particles deposited in the inlet. Vossler et al. (1988) found no loss of nitric acid in Teflon-coated glass impactors. Appel et al. (1988) reported substantial losses of nitric acid in sampling inlets, especially cyclones; but they also reported minimal losses for residence times less than 0.2 seconds. The residence time of the inlets used in this study, at a sampling rate of 12.5 Lpm, is estimated to be < 0.04 seconds, so significant adsorption of HNO_3 on the PTFE/FEP coating is not likely to have occurred. However, adsorption of HNO_3 or SO_2 onto large alkaline particles deposited in the inlets cannot be ruled out. Further research will be needed to accurately determine the fraction of the inlet losses that should be assigned to the coarse-particle or reactive-gas fraction.

TABLE 44. FIELD TEST RESULTS USING FOUR COLLOCATED SAMPLERS*

	Aqueous Concentration, µg/L					Amb. Conc.
Constituent	Samp. 1	Samp. 2	Samp. 3	Samp. 4	Avg.	µg/m³
Coarse-particle nitrate-N						
Inlet	121±0.5	156±0.2	129±2.4	151±1.3	139±17	0.077±12.2%
Impaction disk	241±3.5	234±2.9	252±6.1	240±5.1	242±7.5	0.134± 3.1%
Total	362±3.5	390±2.9	381±6.6	391±5.3	381±13	0.212± 3.4%
Coarse-particle sulfate						
Inlet	168±3.6	205±7.4	147±3.5	182±13.3	176±24	0.098±13.6%
Impaction disk	229±2.5	209±7.1	236±2.6	224± 8.3	225±11	0.125± 4.9%
Total	397±4.4	414±10.3	383±4.4	406±15.7	400±13	0.222± 3.3%
Coarse particle ammonium-N						
Inlet	80	90	70	120	90±22	0.05 ±24.4%
Impaction disk	100	80	100	90	93±10	0.05 ±10.8%
Total	180	170	170	210	183±19	0.10 ±10.4%
HNO_3-N						
1st denuder	491±7	436±4	492±14	438±5	464±32	0.258± 6.9%
2nd denuder	24±0.8	22±0.4	25±0.5	27±0.5	25±2.1	0.014± 8.4%
Net	467	414	467	411	440±31	0.244± 7.0%
HNO_2-N						
1st denuder	284±5	265±5	294±5	268±5	278±14	0.154± 5.0%
2nd denuder	22±0.4	23±0.5	24±0.0	21±1.0	23±1.3	0.013± 5.6%
Net	262	242	270	247	255±13	0.142± 5.1%
SO_2 (as sulfate)						
1st denuder	28382±439	27061±320	28799±498	27481±402	27913±799	15.5 ± 2.9%
2nd denuder	50±2.9	76±6.2	112±2.8	126±6.6	91±35	0.051± 38%
Net	28332	26985	28687	27355	27839±801	15.5 ± 2.9%
NH_3-N	225	235	245	245	238±10	0.132± 4.2%
Fine-particle nitrate-N†	588±4.7	547±8.3	601±4.9	567±11.4	567±24	0.315± 4.2%
Fine-particle sulfate	3724±57	3499±48	3788±46	3626±109	3659±126	2.03 ± 3.4%
Fine-particle ammonium-N	1410	1360	1510	1450	1435±68	0.797± 4.7%

* Ambient air sampled for 24.0 hours at 12.5 Lpm; 10-mL extracts; standard deviations shown in µg/L for individual samples (5 replicates) and 4-sample averages, and as a percentage for average ambient concentrations.

† Collected on PTFE filter; no correction made for volatilization (see text).

The results (Table 44) are comparable with other measurements that have been made in northeastern Kansas, with SO_2 and fine-particle sulfate being the most abundant species. Note, however, that the nitrogen containing species are reported as nitrogen (MW = 14.001), so direct comparisons among the concentrations of nitrogen and sulfur containing species may be misleading. For example, the coarse-particle nitrate concentration is actually 0.939 $\mu g/m^3$ as nitrate, substantially higher than the 0.222 $\mu g/m^3$ concentration of sulfate. Also, the coarse-particle ammonium concentration of 0.10 $\mu g/m^3$ as nitrogen is equivalent to 0.0071 $\mu moles/m^3$, which when compared to the molar concentration of coarse-particle sulfate of 0.0023 $\mu moles/m^3$ reveals that there is actually an excess of ammonium over sulfate and that both ammonium sulfate and ammonium nitrate particles were likely present. This nitrogen enrichment of the coarse particle fraction has been noted by other investigators (Wolfe, 1984; Wall et al., 1988; Cadle and Mulawa, 1988) and the desire to more accurately sample and analyze this nitrogen-enriched fraction was one of the primary motivations for this research.

The analytical precision for nitrite, nitrate, and sulfate in individual samples (5 replicates) was quite good, averaging ± 1.5% for concentrations exceeding 500 µg/L, ± 2.0% for concentrations of 100-500 µg/L, and 3.8% for concentrations below 100 µg/L. These results are in reasonable agreement with the precision data presented in Section 6A, as well as those reported by Stevens et al. (1988a & 1988b). The mass flow controllers used for this test were calibrated at the factory (all on the same date) with an accuracy of ± 1%; but they were cross-calibrated in the laboratory and found to agree to within ± 0.5%, and their specified repeatability (precision) was 0.2%. Furthermore, the precision with which a 10-mL sample can be prepared is ± 0.5%. Hence, the precision of the method for constituents having concentrations higher than 100 µg/L (0.056 $\mu g/m^3$) should have been approximately ± 3%. However, the precision actually observed was slightly but significantly higher (Table 44).

The poorer than expected precision could be due to such factors as sample contamination during handling, true differences in concentration in the air sampled, or variations in flowrate caused by malfunction of the flow controllers or by leaks in the sampling system. Since the analytical results were very precise and the blank values were consistantly low (as discussed later in this section), sample contamination was not considered as a likely cause of the problem. Also, since all four sampling inlets were mounted high in the air at the same height and facing the same direction, it is not likely that the variations among sampling systems were due to differences in the ambient air sampled. This left variations in flowrate as the most likely explanation.

A rank-order analysis of the concentrations of nitrate and sulfate associated with individual sampling-system components (Table 45) lends credence to the notion that variations in flowrate were responsible for the poorer than expected precision. The concentrations of the major sulfate and nitrate species on each component are perfectly rank correlated with the number of the sampling system, with sampler 3 having the highest concentrations in all cases, followed in order by samplers 1, 4, and 2. The

TABLE 45. RANK-ORDER ANALYSIS OF FIELD TEST RESULTS

System Component	Rank Order (1 = Highest) Sampler 1	Sampler 2	Sampler 3	Sampler 4
Impaction filter				
Nitrate	2	4	1	3
Sulfate	2	4	1	3
First Denuder				
Nitrate	2	4	1	3
Sulfate	2	4	1	3
PTFE Filter				
Nitrate	2	4	1	3
Sulfate	2	4	1	3

TABLE 46. SYSTEM AND REAGENT BLANK VALUES FOR THE FIELD TEST

Blank Analyzed	Blank Type*	Concentration, µg/L** NO_2-N	NO_3-N	Sulfate	NH_4-N
Impaction Filter No. 5	S	ND	2.3	4.8***	ND
Impaction Filter No. 6	S	ND	ND	2.0***	ND
Sodium-Carbonate Denuder No. 5	R	ND	ND	ND	NA
Sodium-Carbonate Denuder No. 6	R	ND	ND	ND	NA
Sodium Carbonate Denuder No. 7	R	ND	1.4	ND	NA
Citric-Acid Denuder No. 5	R	NA	NA	NA	30
Citric Acid Denuder No. 6	R	NA	NA	NA	100
PTFE Filter No. 5	R	ND	ND	28	ND
PTFE Filter No. 6	R	ND	ND	31	ND
PTFE Filter No. 7	S	ND	2.5	35	ND
PTFE Filter No. 8	S	6.2	2.0	31	ND
Nylon Filter No. 5	R	1.0	4.0	NA	NA
Nylon Filter No. 6	R	ND	ND	NA	NA
Glass-Fiber Filter No. 5	R	NA	NA	NA	160

* System blanks are those were placed in the sampling system, equilibrated, weighed, and otherwise treated in the same manner as the samples.

** ND = not detected; NA = not applicable.

*** Sulfate was not detected on 3 of 5 replicates for impaction filter No. 5 and on 4 of 5 injections for impaction filter No. 6.

ammonium results deviated somewhat from this pattern, but ammonium was only analyzed in duplicate using a less precise method having higher blank values. Since the same trend was found for all three system components, the pattern is much more likely the result of flowrate variations than imprecise sample dilution.

One possible cause of flow variation is leaks in the sampling system, and tests were conducted to explore this possibility. The couplers used to connect the system components were found to permit very small amounts of air to leak into the system under a 400-mm vacuum, but since the headloss (pressure drop) associated with the inlet and denuders is exceedingly small under normal operating conditions, this was not considered to be a significant factor. However, leaks in the filters packs could indeed be significant, since there is a large pressure drop caused by both the PTFE filter and the Nylon filter, as well as a small pressure drop associated with the coated glass-fiber filter. Tests revealed that filter packs without filters in them occasionally leaked slightly under vacuum, but such leaks could be stopped by placing a light film of silicone grease on the sealing surfaces. Filter packs with filters in them tended to leak under vacuum. Anlauf et al. (1986) have also reported finding leaks in filter packs, and improved filter pack designs are clearly needed, especially in situations where a high degree of accuracy or precision is desired (e.g., when determining deposition velocities using the gradient method).

The blank values associated with the field test results are shown in Table 46. The blank values were generally quite low. The high sulfate blank values for the PTFE filters are insignificant relative to the ambient concentrations of SO_2 typically found in northeastern Kansas, and the ammonium blanks were uncharacteristically high. The low blank values for the oiled membrane filters, which had been exposed to laboratory air for several days (during weight stabilization for gravimetric analysis), were very encouraging. Since the laboratory air was probably contaminated with NH_3, HNO_3, and SO_2 in concentrations exceeding the ambient outdoor air, this is good evidence that silicone oil does not adsorb or react with these gases.

Gravimetric analysis of the TFE impaction disks and PTFE filters was attempted, but the building's air conditioning system failed while the samples were being equilibrated, drastically changing the temperature and humidity in the balance room. The gravimetric measurements were quite inconsistent, so the data were discarded. However, it should be noted that the total mass of the known constituents on the impaction disk was only 25 µg, which cannot be accurately determined using a 5-place balance, since the precision of a 5-place balance is typically ± 25 µg. The gravimetric procedure described in Appendix A is suitable only for much higher concentrations of particulate matter, and it requires additional testing to verify that stable weights can be obtained.

After the PTFE filters were extracted, they were removed from their respective vials, lightly rinsed with reagent water, and then extracted a second time to determine if additional material could be extracted from them. The results for the second extractions, shown in Table 47, show that the first extraction was very thorough. The trace concentrations found in the second extract may be due to mechanical carry over. In hindsight, a similar experiment should have been conducted with the oiled impaction filters; but the heavily soiled impaction filters appeared to be perfectly clean after the first extraction, and the possibility that they might contain additional extractable ions was not considered at the time.

TABLE 47. ANALYTICAL RESULTS FOR RE-EXTRACTED PTFE FILTERS

	Concentration, µg/L**			
	NO_2-N	NO_3-N	Sulfate	NH_4-N
PTFE Filter No. 1	4.2	3.3	11	20
PTFE Filter No. 2	ND*	3.6	22	20
PTFE Filter No. 3	2.2	3.2	19	20
PTFE Filter No. 4	5.0	3.3	14	10
Avg.	2.9	3.4	17	18
System Blank Avg.	3.1	2.3	33	ND
First Extract Avg.	8.1	578	3692	1435

* ND = not detected

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APPENDIX A

PROCEDURE FOR USE OF THE GLASS-IMPACTOR DENUDER-TUBE FILTER-PACK SAMPLING SYSTEM

A. Preparation of Coating Reagents

1. Sodium carbonate (for adsorption of HNO_3, HNO_2, SO_2, and SO_3)
    a. Add 10.0 gm anhydrous Na_2CO_3 to 400 mL reagent water in a 1000-mL volumetric flask.
    b. Add 10.0 gms glycerol.
    c. Dilute to 1000 mL with HPLC-grade methanol.
    d. Let stand about 15 minutes to equilibrate (off gas).
    e. Do not store in a flask with a fritted glass stopper, since the alkali may "freeze up" the stopper.

2. Citric acid (for adsorption of NH_3)
    a. Add 1.00 gm high quality citric acid to 100 mL methanol.
    b. Do not breathe on or into the reagent (breath contains NH_3).
    c. Prepare fresh daily.

B. System Preparation

1. Bent-tube inlet and glass impactor nozzle
    a. Soak in ~0.1M $NaHCO_3$, thoroughly rinse with reagent water, dry, and tightly cap off both ends.
    b. If soiled, gently wash with soap and water, rinse thoroughly with tap water, then proceed as described in part a.

2. Impaction disk and filter
    a. Remove excess oil from the TFE impaction disk (if previously used) with a clean tissue (Kimwipe).
    b. Place the impaction disk in a clean 50-mL polypropylene tube, add about 15 mL of reagent-grade pentane, vortex mix 30 seconds, sonify 5 minutes, vortex mix 30 seconds, and discard the pentane. (NB: the disk cannot be left in pentane for more than about 30 minutes or it will begin to swell.)
    c. Repeat step "a" substituting 0.1M $NaHCO_3$ for pentane.
    d. Rinse the disk thrice in reagent water, vortex mixing during the last rinse.
    e. Dry the disk in a stream of high-purity nitrogen.
    f. Place a 13-mm, 0.4-µm-pore-size polycarbonate filter on the clean disk and place 5 µL of silicone oil on top of the filter. Allow the oil to wick onto the filter. Store the prepared impaction disk in a dust-proof container.

g. Equilibrate the disk (with oiled filters) in the balance room for 24 hours or to constant weight, weigh to the nearest 10 µg (using the five-place balance), and place in the dust-proof holder for transport to the field. Maintain the disk surface in a horizontal position at all times after oil has been applied. (If gravimetric analysis is to be omitted, the equilibration and weighing steps may also be omitted.)

3. Denuder tubes
   a. Rinse denuder tubes and end caps twice with 10-15 mL of 1% Na_2CO_3, then thoroughly rinse them with reagent water, being especially careful to clean the hollow pedestal in the denuders used to mount impaction disks. Be sure to remove the TFE-coated rubber seals from the end caps and rinse the backsides of the seals and the exposed portions of the end caps.
   b. Cap one end of each denuder tube and pour 10 mL of the desired coating reagent into the tube. Rotate denuder for about 30 seconds to coat the entire tube evenly, then decant excess.
   c. Dry each tube by running high-purity nitrogen through the tube while rotating it. Be sure both ends and the interior of the pedestal are well dried. Use a fume hood to avoid inhaling methanol vapor.
   d. When the denuder is dry, tightly cap off both ends with clean, dry end caps.

4. PTFE filter (MSI MicronSep, 1.0 µm)
   a. Condition the filter at constant temperature and humidity.
   b. Weigh the filter to the nearest 10 µg, then place it in a labelled petri dish. Use gloves and teflon-tipped tweezers to avoid contaminating the filter.

5. Nylon Filter (MSI MicronSep, Magna, Nylon 66, 1.2 µm)
   a. Soak each Nylon filter in IC eluant (50 mL in a polypropylene tube) for at least one hour, remove the filter with clean forceps, and rinse it thoroughly with reagent water.
   b. Dry the filter as described below in part 7.

6. Glass-fiber filter (Gelman AE)
   a. Rinse thoroughly with reagent water, then dip in citric-acid coating solution and drain excess.
   b. Dry the filter as described below in part 7.

7. Filter Drying
   a. Scrupulously clean all of the filter pack components, especially the surfaces touching the filters. Add a thin film of silicone high-vacuum grease to the sealing surfaces, if needed to achieve an air-tight seal. Rinse thoroughly with reagent water. Reassemble using forceps to handle internal components so that no salts are transferred to them.
   b. Assemble the filter pack, placing the Nylon filter on the upstream stainless-steel support plate and the citric-acid-coated glass-fiber filter on the downstream support plate.

c. Attach a glass connector to the upstream end of the filter pack and to a tank of high-purity nitrogen with the pressure regulated to 2 psi.

d. Attach the filter-pack inlet to a regulated source of nitrogen gas and the outlet to a vacuum source and regulate the flow of nitrogen with a rotameter to about 10 Lpm.

e. After the flow stabilizes, continue drying for 10 minutes.

f. When filters are dry, tightly cap off both ends of filter pack without twisting the inner parts (which may tear the filters).

C. System Assembly and Use

1. Assembly

a. Place the Nylon filter on top of the citric-acid-coated glass-fiber filter on the downstream support plate. Place the preweighed PTFE filter on the upstream support plate, then tightly close the filter pack and cap the upstream end and seal the other with parafilm) for transport to the field. Avoid twisting the inner parts. If the PTFE filter will not lie flat, wet it with 100 µL of methanol during assembly.

b. In the field, connect the citric-acid-coated denuder tube to the filter pack, connect two sodium-carbonate-coated denuder tubes to the citric-acid-coated denuder tube, and mount the assembly on the support bracket. Be sure the open ends of the denuder tubes face downstream. Carefully insert an impaction disk into the pedestal on the influent end of the first sodium-carbonate denuder tube, maintaining the surface of the disk in a horizontal position and leaving the top of the disk flush with the end of the denuder. Connect the glass impactor (fitted with a glass bent-tube inlet) to the sodium-carbonate-coated denuder tube, using the special coupler provided.

2. Use

a. Raise the sampling system to the designated sampling height. Connect the system to the vacuum line and carefully set the mass flow controller to achieve the desired flowrate of 12.5 Lpm. When multiple samplers are used, use a symmetrical sampling manifold.

b. Check the flowrate at the end of the sampling period to be sure it has not changed.

c. At the end of the sampling period, disassemble the system immediately, tightly capping off each component with clean caps (stored tightly wrapped in foil) for transport back to the laboratory. The impaction disk should be placed in the holder and carefully and gently transported ~~back to the laboratory in~~ an upright position so that no spillage of the oil occurs.

D. Preparation of Samples for Analysis

1. Bent-tube inlet and glass-impactor nozzle

a. Leaving the bent-tube inlet tightly attached to the inlet of the glass impactor and having tightly capped the bottom of the glass impactor nozzle (such that water cannot escape from the jet nozzle), place 10.0 mL of fresh reagent water and 100 µL of eluant concentrate (110-fold strength eluant solution) into the bent-tube inlet, cap the inlet, and shake gently for several minutes, making sure the water contacts all exposed surfaces.

b. Decant the extract into a prewashed 15-mL polypropylene tube, fill two 1.5-mL vials for NH_4-N analysis, and store the remainder for IC analysis.

2. Impaction filter
   - a. Equilibrate the impaction disk (support and filter) in the balance room for 24 hours or to constant weight, weigh it to the nearest 10 µg, and then remove the filter and place it in a scrupulously cleaned 15-mL polypropylene tube and tightly cap the tube. For sampling times of less than 24 hours or when low mass loadings are expected, omit gravimetric analysis.
   - b. Add 3 mL of pentane to the 15-mL polypropylene tube containing the filter and cap the tube tightly. Immediately vortex mix for 20 seconds, sonify for 1 minute, and vortex mix for 10 seconds.
   - c. Immediately add 10 mL of fresh reagent water and 100 µL of eluant concentrate and cap the tube tightly. Vortex mix for 20 seconds.
   - d. Take a clean disposable pipet (rinsed with reagent water) and suction off the pentane layer, leaving as much of the reagent water as possible.
   - e. Fill two 1.5-mL sample cups for NH_4-N analysis and store the remainder for IC analysis.

3. Denuder tubes
   - a. Add 10.0 mL of reagent water to each denuder tube and 100 µL of IC eluant concentrate to each sodium-carbonate denuder tube. Cap the tubes and shake them well, rotating them to completely extract the coatings.
   - b. Decant each extract into a prewashed 15-mL polypropylene tube and cap tightly.
   - c. Add two drops of 3.0% H_2O_2 to the extract from the sodium-carbonate denuder tubes to convert sulfite to sulfate prior to IC analysis.

4. PTFE filter
   - a. Place the soiled filter in a labelled petri dish and condition it for 24 hours or to constant weight at constant temperature and humidity. Weigh the filter to the nearest 10 µg. Use gloves and clean PTFE-tipped tweezers to avoid contaminating the filter.
   - b. Place the filter in a pre-washed 15-mL polypropylene centrifuge tube, add 10.0 mL of fresh reagent water from a clean pipet and 100 µL of IC eluant concentrate. Sonify the sample for 5 minutes with the filter completely submerged.

5. Nylon and glass-fiber filters
   a. Place each filter in a prewashed 15-mL polypropylene tube, add 10.0 mL of reagent water and 100 µL of IC eluant concentrate, cap tightly, then sonify for 5 minutes. Be sure each filter is completely submerged.
   b. Remove the glass-fiber filter using clean teflon-tipped tweezers.
   c. If the glass-fiber-filter extract is turbid (from fiber particles), filter the sample through a prewashed 13-mm glass-fiber filter using a prewashed 20-mL syringe and a syringe-type filter holder. discard the first mL of filtrate and place the remainder in a 15-mL polypropylene tube.

E. Sample Analysis

1. All samples
   a. Refrigerate at 4°C until analysis; analyze as soon as possible.
   b. Be careful not to cross-contaminate samples or to introduce anything into the samples that might interfere with subsequent analyses.
   c. Save any remaining sample until satisfied that the results are accurate; then discard remainder.

2. Analytes
   a. Analyze the sodium-carbonate denuder-tube and Nylon-filter extracts for nitrogen- and sulfur-bearing anions only.
   b. Analyze the citric-acid denuder-tube and citric-acid-coated glass-fiber-filter samples for NH_4-N only.
   c. Analyze the PTFE-filter, bent-tube inlet, and impaction filter samples for anions and NH_4-N.

3. Nomenclature for sample identification

IN	Impactor inlet
IF	Impaction filter
SC	Sodium-carbonate-coated denuder tube
CA	Citric-acid-coated denuder tube
TF	PTFE filter
NY	Nylon filter
GF	Citric-acid-coated glass-fiber filter